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THE EFFECT OF ANNEALING UPON THE PHYSICAL PROPERTIES, AND THE MICROSTRUCTURE OF A LOW CARBON STEEL.

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THE enormous demand for low carbon steel for structural purposes, plate, tubing, and its many varied uses, offers great temptation for the manufacturer to allow almost any kind of material to pass through the mills without paying particular attention to the condition in which it appears upon the market. That the manufacturer does occasionally submit to the temptation to work the mills beyond their capacity, is shown in the failure of the metal to meet certain physical requirements. That these failures are not more frequent is to be greatly wondered at, and it goes to show under what excellent control the steel plants are held. This occasional failure, however, makes it necessary to study carefully the conditions, which, if not strenuously adhered to, will produce steel which will not only give trouble to the manufacturer himself, causing loss of time and perhaps material, but may also be a source of trouble to the buyer, and perhaps a source of danger to the public. The buyer, in order to protect himself, usually subjects the material to certain physical tests which tell him whether the steel has the requisite strength. This determination of tensile strength was considered for a long time as entirely satisfactory and all

that was necessary, but the presence in the steel of certain elements, such as phosphorus and sulphur, which were supposed to have an injurious effect on the physical properties, led the cautious buyer to test his steel both physically and chemically. It is a well known fact that two pieces of steel having identically the same composition may have entirely different physical properties. This marked difference in physical properties was found to be due to the difference in heat treatment. We are able to say of any piece of steel, that its physical properties depend primarily on its chemical composition, and secondly, on the heat treatment to which it has been subjected. If we know, then, the chemical composition and the heat treatment, we should be able to predict the physical properties.

The query now arises, if we have two steels of the same composition but of different physical properties, is there any means of knowing the heat treatment? Fortunately, this can be answered in the affirmative. It has been shown by Sorby, Osmond, Stead, Ridsdale, Sauveur, and other investigators, that there is a direct relation between the heat treatment and the microstructure of steel. A study of the microstructure, together with the physical properties of metals, has given rise to the science which has been designated by the name Metallography.[1] For some varieties of steel and many alloys, these relations have been very carefully worked out, and this information has added enormously to our knowledge of the properties of steel and other alloys. It was the object of this investigation to start with a steel of known composition and to study carefully the heat treatment, and how it would effect the physical properties and the microstructure. Having this information established for this class of material under normal conditions, we have certain standards from which to draw our conclusions. This, however, does not give all of the information which we desire, as it is well known that work, such as rolling, hammering, etc., has a decided influence on the physical properties. This portion of the work, however, was impossible for us to carry out, and we present the paper in its present form with the hope that the subject will be of sufficient interest to be completed along similar lines by some practical metallurgist. The investigation is incomplete in another sense, viz.: that we have heated our specimens to a certain definite temperature and allowed the metal to

[1] For the elements of the subject see "The Metallographist."

cool from that temperature, but have not held the steel for any length of time at the temperatures to which it was heated. Our cooling was carried out slowly enough, as will be shown later on, for complete crystallization to take place, but according to Stead's[1] experiments, coarse granulation takes place by holding the sample for some time at about 700° C. This portion of the work is now in progress, and it is hoped to bring forth our completed results later. The material selected for this purpose was a low carbon steel which was kindly furnished by the National Tube Company, of McKeesport.

The steel which we used is generally classified as "extra mild steel." Many investigations have been conducted on mild steel, but none of the investigators have followed exactly the same manner of work. Before proceeding to the experimental work it will be necessary to review briefly the work which has already been done on mild steels.

Until the publication in 1898, of Mr. Stead's paper on "The Crystalline Structure of Iron and Steel," it was tacitly assumed that all grades of steel, whether soft or hard, followed the general laws of structure, as enunciated by Chernoff and Brinnel. These two investigators were the first to formulate any laws connecting the heat treatment and the structure. Both of them experimented principally upon steels of medium hardness, about 0.3 per cent. of carbon. Their conclusions in regard to the structure were based upon the appearance of the fractures.

Chernoff[2] summarized his conclusions as follows: Steel on solidifying has a crystalline structure. This may be prevented:

1. By simple reheating to a cherry red when an ingot with a coarse structure will suddenly be transformed into a fine-grained and strong product.

2. By hammering at a high temperature, and continuing the work down to a low temperature, to a certain point, varying with different steels, below which the metal preserves its whole power of resistance.

3. Rapid cooling of the cast metal destroys the crystalline structure.

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[1] The Crystalline Structure of Iron and Steel. J. E. Stead. J. Iron and Steel Inst., 1898, No. 1, 145.

[2] The Structure of Cast Steel Ingots. Proc. Inst. of Mech. Eng., January, 1880; translated from the Russian by Mr. W. Anderson.

The Manufacture of Steel and the Mode of Working It. Proc. Inst. of Mech. Eng., April, 1880; translated by Mr. W. Anderson.

Chernoff points out the important fact that the higher the percentage of carbon, the lower is the point below which no change in structure occurs.

Brinnell's[1] conclusions follow along the same line as those of Chernoff, but are expressed more in detail. A few abstracts from his work, having a special bearing upon the subject, are given below:

1. Whenever steel loses its crystalline structure, other than by mechanical work, the change of texture will be found to occur simultaneously with the transformation of cement into hardening carbon, or *vice versa*, and the change will be complete only in the event of the carbon being converted by heat from cement into hardening carbon.

2. In order to effect the transformation of hardening into cement carbon, in a steel heated to a white heat, it must be allowed to cool slowly to a lower temperature than that necessary to change cement into hardening carbon.

3. If hardening carbon, in heating or cooling, is converted completely or largely into cement carbon, a crystallization occurs, yielding a fracture the coarser, as the former texture of the steel was crystalline.

4. The crystallization of steel requires a certain amount of time as well as a certain amount of heat. If the duration of the cooling process is cut short by quenching in water, the development of crystallization is partly or wholly prevented.

With regard to the development of a coarse crystallization, Brinnell says that on heating the steel to a point W, say 750°, the size of the granules increases with the temperature, the coarsest being obtained by heating to the highest temperature, and the structure remains coarse whether the steel is quenched or cooled slowly from the temperature.

Within the last few years several important articles have appeared dealing with the effect of heat treatment upon soft and extra soft steels, the results of which seem to be quite different from those of the earlier experimenters upon medium and hard steels. These later researches are also characterized by the use of the microscope for the examination of the structure instead of the naked eye and fractured surfaces.

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[1] The Changes in the Texture of Steel on Heating and on Cooling. Abstracted in J. Iron and Steel Inst., 1886, No. 1, 365.

From his microscopic work upon soft steels and pure iron, Mr. Osmond[1] came to the following conclusions in regard to heat treatment:

1. Steel with 0.02 per cent. C. "It would seem that the structure of pure iron is almost independent of the temperature and the rate of cooling."

2. Steel with 0.14 per cent. C. "In proportion as the temperature of reheating is raised, other things being equal, the polyhedrons of ferrite enlarge, slowly at first, and keeping their forms, then more rapidly, until at 1,000° they become irregular and tend to lengthen into groups of juxtaposed bands. The pearlite generally remains exterior to the arrangement of ferrite, and stratifies in seams."

The most important articles on this subject that have yet appeared have been by Mr. J. E. Stead.[2] His first paper on "The Crystalline Structure of Iron and Steel" revolutionized our ideas upon the effect of heat treatment on soft steels, and showed that they followed laws of structure which so far have not been found to apply to carbon steels. Among the conclusions that Mr. Stead draws, we have selected the following, which have a bearing on the present work:

1. Granules and crystals should not be confused, for although a granule is built up of crystals, its external form is not crystalline, as it takes its shape from its surroundings. It is an allotrimorphic crystal, or more simply, a grain.

2. Grains formed in the solidification of liquid metals are large or small according to whether the freezing is rapid or slow, and they take their form from their surroundings, and this is most irregular, owing to natural interference.

3. In carbonless pure irons or steels of fine grain produced by either forging or certain heat treatment, the grains increase in size, slowly at 500° C., and more rapidly at between 650° to 750°, and it is possible by heating at about 700° for a few hours to develop granular masses of exceeding coarseness. At 900° the granules again become small, and heating to 1,200° apparently does not change them.

4. Granules in carbon steels 0.20 per cent. to 1.20 per cent. carbon do not grow in size by long continued heating at 700°, but they increase in size slowly at first, and then more rapidly with each increment of temperature above 750° C., the change point varying with the carbon. When, however, coarsely granulated steel is reheated again a little above 700° to 750°, the coarse structure vanishes.

[1] Bull. Soc. d'Encouragement pour l'Industrie Nationale [5] 10, 476. [2] See above.

5. In steels of from 0.10 per cent. to 0.15 per cent. carbon containing the pearlite in widely separated areas, on heating and quenching from about 750° the large ferrite grains are not broken up, and the carbon apparently does not expand or diffuse beyond the original area, but when heated to 850° and slowly cooled the carbon areas are found as a number of smaller segregations, and where the carbon has diffused the ferrite is found in small grains.

Mr. Stead's second paper on "Brittleness Produced in Soft Steel by Annealing,"[1] follows the line of his previous paper, but brings out a number of new facts. Among other points, he distinguishes two kinds of weakness, viz:

1. Intergranular weakness which occurs when the grains are imperfectly cohesive or are surrounded by a brittle envelope.

2. Cleavage weakness which occurs where the grains are so oriented that the component crystals are all in the same phase. He explains the brittleness sometimes observed in annealed plates by saying that the rolling causes a tendency to such orientation, and that annealing develops this tendency.

Mr. Stead suggests that at about 900° for soft steel γ-iron is formed, and coincident with it the structure is refined. The results of the present investigation bear out this conclusion. Mr. Stead also makes the pertinent suggestion that the banded or laminated structure of the ferrite, observed in overheated steel, provided there is no intergranular separation, is a remarkably strong one.

Shortly after the publication of Stead's papers, Ridsdale published an article on "Brittleness in Soft Steel,"[2] containing much valuable material. He draws the following conclusions, "In order to avoid brittleness:

1. "There should not be too high an initial temperature nor 'soaking' at a high temperature for a long time."

2. "Work should be continued down to red heat, but not to a blue heat."

3. "If work has been continued unavoidably to near blue heat, there should be no chilling, but slow cooling, and where possible subsequent heating, if only for a short time, to cherry redness. Also there should be absence of jar or vibration whilst cooling through the blue heat."

[1] J. Iron and Steel Inst., 1898, No. II, 137.
[2] J. Iron and Steel Inst., 1898, No. I, 220.

A year later, in 1899, Mr. Ridsdale published a very comprehensive paper on "Practical Microscopic Analysis for Use in the Steel Industries."[1] He emphasizes strongly the importance of soft steels, and the neglect which they have suffered at the hands of the metallographists. His conclusions, which are derived from the study of numerous specimens of steel made by various processes and makers, are illustrated by photographs at 50 diameters.

His conclusions may be stated as follows:

1. Normal steel, work continued to a low red. The structure is regular and homogeneous, the grains small and ill-defined.

2. Normal treatment and abnormal composition. The structure is in general the same as the preceding. Phosphorus tends to enlarge the grain slightly.

3. Normal steel heated too long or to too high a temperature. This shows an outer carbonless band with large grains, or if actually burnt, a separation of the grains.

4. Normal steel worked at too low a temperature or through a blue heat. This shows a strained structure with distinct flow lines. There is a breaking up of the surface grains and a loosening or actual rupture of the grain junctions.

"In general," Ridsdale says, "outside of normally treated specimens, the effect of heat treatment far outweighs that of composition."

Morse,[2] who worked on a steel containing 0.34 per cent. carbon, finds a diminution in tensile strength when held between 650° and 750°, an increase from the latter point up to 900°, and a falling off from 900° to 1,200°. Beyond 1,200° the tensile strength rises again. The area of the grain increases up to 600°, falls to a minimum at 900°, and then increases rapidly. The author notes the occurrence above 1,000° of the banded or ramified structure noted by Stead, and he reaches the same conclusion as to its being a strong structure.

In regard to the existence of a point of change in the physical properties at a temperature above 1,000°, there are several articles which deserve mention. Ball published an article "On the Changes in Iron Produced by Thermal Treatment,"[3] in which he investigated the effect upon the tensile strength and magnetic properties of a steel containing about 0.10 per cent. carbon when slowly cooled, and when

[1] J. Iron and Steel Inst., 1899, No. II, 102.

[2] Trans. Am. Inst. Min. Eng., 1900, 29.

[3] J. Iron and Steel Inst., 1890, No. I, 85; 1891, No. I, 103.

quenched from various temperatures. The steel shows three critical points, one at 660°, another at 900°, and a third at 1,200°, at which latter point the magnetic and physical properties reach a maximum.

Recently Roberts-Austen[1] has published a cooling curve of electrolytic iron which shows an evolution of heat at a temperature of 1,132°, and this he identifies with the point of maximum tenacity observed by Ball. This upper critical point coincides fairly closely with the second point of maximum tenacity observed in the present series of experiments.

Experimental.

The material which was used for these experiments was a low carbon, acid Bessemer steel of a commercial grade, and was kindly furnished by the National Tube Company, of McKeesport, Pennsylvania. It represents the average material of this grade turned out by the company for the manufacture of pipes and tubes.

The chemical analysis was as follows:

C = 0.07. S = 0.058. P[2] = 0.10. Mn = 0.32. Oxides = 0.25.

The carbon and manganese were determined by colorimetric methods.

The heat treatment in the mill, was approximately as follows: The ingots were subjected, in the soaking pits, to a temperature of 1,000° to 1,200°. They entered the roughing train at probably over 1,000°, and the mechanical work was continued to a full red heat. The specimens, thirty in number, were all cut from plates rolled from the lower two-thirds of the same ingot, and came in the shape of bars 18 inches long, $1\frac{3}{4}$ to $2\frac{1}{4}$ inches wide, and $\frac{3}{8}$ inch in thickness. The edges were planed. In order to heat the specimens uniformly and to a temperature which could be accurately measured, the usual forms of furnaces were found inconvenient. At the suggestion of Mr. C. L. Norton,[3] a furnace heated by electricity was constructed and was found to answer all of the requirements most admirably.

The general principle on which the furnace is based is that when a conductor is traversed by a current, heat is developed according to Joules's law, $W = C^2R$. The resistance of the wire, however, increases

[1] Metallographist, No. II, 186.

[2] Although high, the phosphorus seems to have had no effect on the size of the grain.

[3] Complete details in regard to this and other forms of electric furnaces used in the heat laboratory, will appear in a separate article by Mr. Norton.

as the temperature rises, and as the loss of heat by radiation also increases with the temperature, it may be seen that for each difference of potential between the terminals there is a certain maximum temperature which may not be exceeded. The rise in temperature for 110 volts is shown by the curve in Figure 1. By the use of 220 volts, however, the temperature may be readily raised to 1,300°.

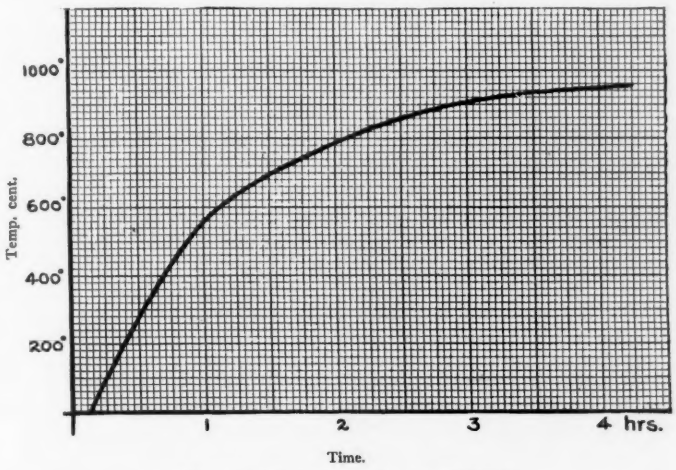

FIG. 1. — HEATING CURVE OF FURNACE.

The furnace consisted of a cylindrical muffle 20 inches long and $3\frac{1}{4}$ inches in diameter wound with about 72 feet of No. 29 platinum wire, and inclosed in an insulating jacket of about 15 inches external diameter, and 30 inches long. The muffle was made by taking three clay porous cups, sawing the bottoms off two of them and placing the three in line so as to form a hollow cylinder closed at one end. The bottom of the third cup was perforated by a $\frac{3}{4}$-inch hole so that a tube could be inserted and a neutral gas, such as nitrogen or carbon dioxide, drawn through to prevent oxidation of the specimens. It was not found necessary, however, in these experiments.

The three sections of the muffle were wound independently, each with about 24 feet of No. 29 platinum wire, and the ends were brought out to six binding posts on the outside of the furnace. The insulating jacket consisted of two pieces of asbestos pipe cover, one 12-inch piece outside, and a 4-inch piece inside. The spaces between the two pipe

covers, as well as between the inner pipe cover and the muffle, were packed with fibrous asbestos. The whole furnace was supported in a wooden cradle, and is shown in section by the accompanying sketch, Figure 2.

The electric current was taken from the three wire mains of the incandescent circuit by the three coils in parallel. For temperatures below 800°, 110 volts were used, and for temperatures above 800° the

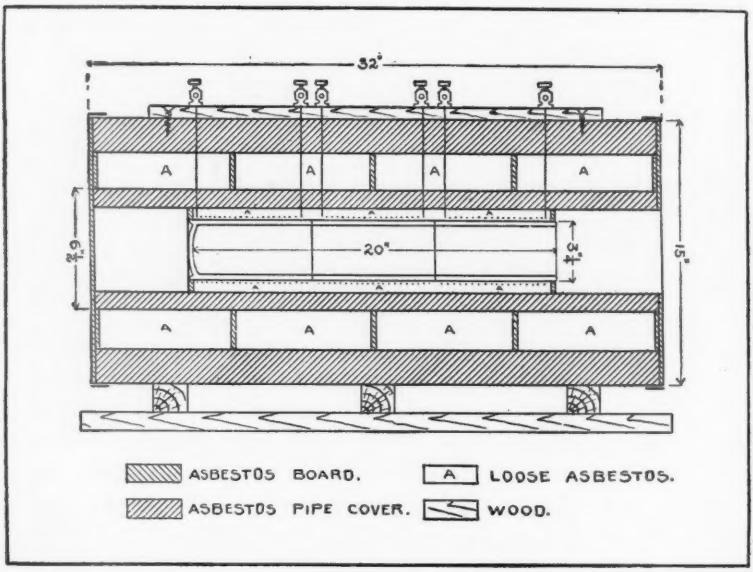

Fig. 2
Section of Furnace.

furnace was heated to 800° on the 110 volt circuit, and then shifted to the 220 volt circuit.

The efficiency of the furnace was very good indeed. With a difference of potential of 110 volts the current passing varied from 10 amperes when cold, to 6.5 amperes when hot, and the furnace could be heated to 800° in about one and one-half hours. (See Figure 1.)

The pyrometer used was of the LeChatelier thermo-electric type. The junctions consisted of a platinum, and a platinum 10 per cent. iridium wire, and were protected by perforated clay tubes The junction was simply laid on top of the bar in the furnace, but the

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heating was so gradual that this represented very closely the actual temperature.

The galvanometer was a four-coil, astatic instrument suspended from the ceiling to prevent vibration. The source of light was a 32 C.P. lamp, a narrow adjustable slit being interposed between it and the mirror. The image of the slit was thrown onto a ground glass strip graduated in millimeters.

The pyrometer was calibrated against the following substances:

Boiling water, 100° C.	Boiling naphthalene, 219°.	Boiling sulphur, 445°.
Freezing aluminium, 660°.	Freezing gold, 1,072°.	

The temperatures above 1,072° were obtained by extrapolation on the calibration curves. The general arrangement of furnace, galvanometer, and wiring is shown in the photograph of the apparatus, Figure 3.

The treatment of the specimens was carried on as follows: A bar, numbered at each end with its serial number, was placed in the furnace. Upon it, and extending to a point one-third the length of the bar was placed the pyrometer junction. The mouth of the muffle was then closed with a wad of loose asbestos, and the heating was begun. The current was turned on at 110 volts with the coils in parallel until a temperature of 800° was reached, when 220 volts was turned on and the furnace heated to the desired temperature. The circuit was now broken, and the maximum temperature recorded. The bar was allowed to cool in the furnace, and after 24 hours, at the end of which time it was still at a temperature of 80° to 100°, was removed. All the bars except Nos. 23 to 27 inclusive, were allowed to cool in the furnace. The latter bars were removed from the furnace just after reaching the maximum temperature and thrown into a box of sand and allowed to cool naturally, reaching the atmospheric temperature in a couple of hours. The furnace was so well protected from radiation that the specimens which were allowed to remain in the furnace were cooled extremely slowly.

The bars, after the heat treatment, were machined for a space of about 12 inches in the middle of the bar to remove the scale and allow an accurate measurement of the cross section of the specimen. After measuring the cross section, the bars were marked for the elongation in 5 inches, and broken in a testing machine.

The testing machine used was a 50-ton Olsen arranged to be run by an electric motor. With the motor running at a constant rate the

load rose rapidly at first, and then slowed up suddenly as shown by a drop of the beam. The stress at which this occurred was taken as the elastic limit, though its accuracy is probably questionable to the extent of 1,000 pounds. After the elastic limit was passed, the piece began to elongate more rapidly, and the load to rise more slowly up to a maximum stress, beyond which the piece began to draw down under a diminishing load. The maximum load was recorded as the ultimate strength of the material. As the piece drew down, two lines of greatest stress, forming a St. Andrew's cross, showed themselves by faint depressions across the bar. These depressions enlarged until the fracture occurred, beginning at the centre and extending to the sides. This mode of fracture, which was characteristic of all the specimens, was beautifully shown by specimen No. 10 with which the machine was stopped just after the middle had parted, and before the break had reached the edges. The fractured bars were placed end to end, and the elongation was measured and recorded. Owing, however, to the way in which the bars parted, the ends could not be placed in perfect contact, and there is consequently some uncertainty in the accuracy of the percentage of elongation.

From the facts obtained in the above described manner, the following data were calculated:

1°. Temperature from which annealed.
2°. Maximum load, pounds per square inch.
3°. Elastic limit, pounds per square inch.
4°. Elongation, per cent. of in 5 inches.

The tabulated results are given in the table, and are shown graphically in Figure 4.

The specimens for microscopic examination were cut from the ends of the fractured bars, and numbered with the serial number. A section, the thickness and width of the bar and 1 inch long, was sawed from a point 3 inches from the end of the bar. This was in order to secure uniformity of heating, and at the same time be sure that the section had not been distorted by the stress during pulling.

The small block so cut was then planed and filed down $\frac{1}{16}$ inch on the flat surface to remove all surface injuries. The specimen was then bevelled on the upper edges and ground on three grades of emery cloth, Nos. 80, 100, and 120, and four grades of "Rupert's" French emery paper, Nos. 10, 1, 0, and 00. This left the specimen with

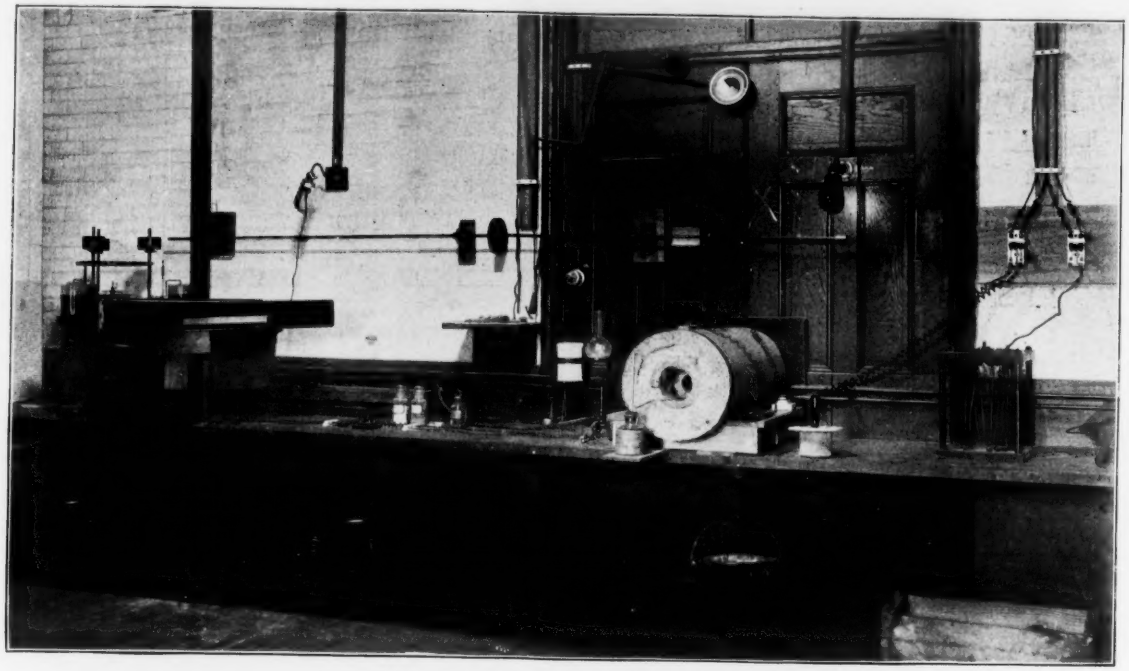

FIG. 3. — FURNACE, PYROMETER, ETC.

TABULATED RESULTS SHOWN GRAPHICALLY IN FIGURE 4.

Specimen number.	Temperature. (Degrees C.)	Area.	Tensile strength. (Lbs. per sq. in.)	Elastic limit (Lbs. per sq. in.)	Elongation in 5 inches. (Per cent.)
1	647°	.5670	56,660	38,790	31.0
18	703	.5827	55,620	37,760	32.2
2	764	.5767	55,690	38,150	31.2
6	765	.5740	56,570	38,320	29.0
4	805	.4953	55,880	38,370	29.8
16	806	.6829	55,000	35,870	28.4
15	817	.6149	55,310	35,780	31.6
8	844	.5768	55,470	38,140	30.6
19	850	.6063	56,790	37,930	30.6
3	889	.5923	59,120	40,520	30.0
11	901	.5920	55,280	38,010	33.2
17	914	.4388	58,750	38,130	....
14	939	.7077	57,110	40,260	33.6
5	939	.5706	58,120	40,310	....
9	950	.6002	57,760	39,980	32 0
22	951	.5244	56,300	36,230	30.6
7	988	.4363	57,530	41,260	28.4
21	990	.5907	56 690	38,920	28.2
28	1,041	.6078	57,190	37,020	31.2
10	1,042	.6538	56,840	38,230	31.0
12	1,075	.6134	58,760	39,130	29.8
29	1,117	.5599	59,770	41,080	30.6
13	1,143	.4831	58,600	39,340	29.8
20	1,247	.5667	53 280	21,170	31.2
[1]23	695	.6764	58,880	43,610	32.5
[1]24	805	.7256	58,530	38,600	32.5
[1]27	891	.6089	60,150	39,000	29.0
[1]26	990	.6355	60,530	36,980	....
[1]25	1,247	.5855	58,100	35,870	30.6

[1] Specimens 23 to 27 inclusive, were rapidly cooled.

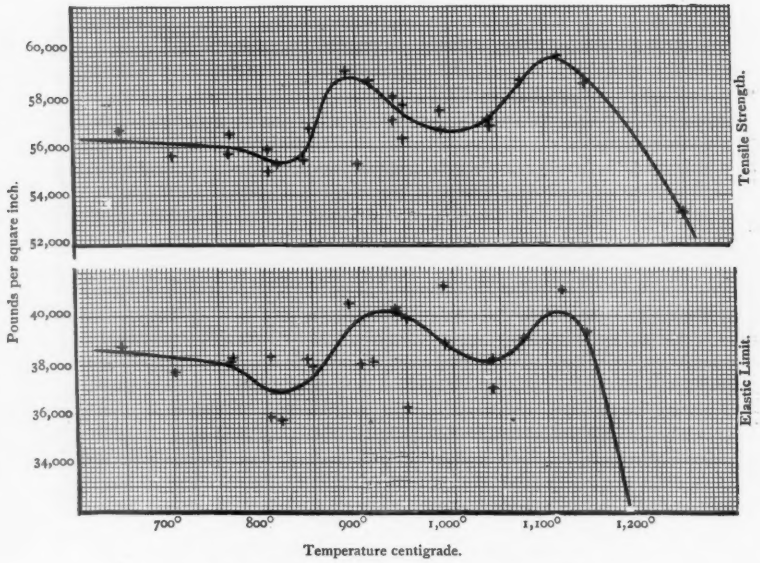

FIG. 4. — CURVES OF TENSILE STRENGTH AND ELASTIC LIMIT.

a dead smooth surface ready for the final polishing, which was done with the finest jeweller's rouge and water upon wash leather stretched on a square tile. The polishing was continued until the specimen was entirely free from scratches and had attained a mirror-like surface.

During the progress of the polishing the specimens were examined at intervals under the microscope. When the scratches were all removed they showed a ground mass of ferrite with small yellowish markings of pearlite unevenly distributed over the field. The pearlite stood out slightly in relief due to its superior hardness. This is shown in Figures 5 and 6. The uneven distribution of the pearlite was quite noticeable even to the naked eye, the block presenting a banded or moiré appearance. Under the microscope the carbon was seen to be highly segregated, some areas being thickly strewn with the pearlite, while others showed only scattered particles.

When the polished specimens had been examined they were etched. The best results were obtained by immersing one end of the specimen in 10 per cent. nitric acid for 30 seconds, and washing first with running water and then with alcohol. The surface was dried by warming

gently. The etched specimens showed very clearly the granular structure of the steel, the joints between the grains being well developed. It is well known that erroneous results are likely to follow the use of nitric acid as an etching medium, but after trying many other agents with indifferent success, it was decided to use nitric acid uniformly throughout the series.

The microscope used was one made by Reichert, of Vienna, especially for metallographic work. It was fitted with an adjustable mechanical stage, vertical illuminator, and iris diaphragm. The field was illuminated by means of a 16 C.P. incandescent lamp placed 18 inches from the microscope. A 3-inch bull's-eye condenser was interposed between the two.

After the preliminary examination the specimens were photographed. The camera for this purpose was the vertical type, and was used with the eye-piece in the microscope just as for eye examination. The ground glass screen was provided with a small circle of clear glass in the centre, and the microscope was focussed by placing a low-power eye-piece, with the ocular lens removed, upon it, and focusing its smaller field. The exposure varied from 20 to 25 minutes. The photographs were taken at 84 diameters, and are reproduced at 73 diameters.

Discussion of Results.

After the specimens had been heated they were, as a rule, covered with a greater or less amount of scale. Those heated to below 750° had a thin powdery coating of red oxide upon them, readily removable with the finger. The specimens heated to above 750° had a coating of black magnetic oxide varying in thickness from the thinnest possible film at 800°, to a thirty-second of an inch at 1,200°.

The machining of the specimens gave no indication of the temperature to which they had been heated, even the 1,247° specimens were apparently uninjured. The first difference in behavior was noted when the tensile tests were made. The specimens heated to below 1,200° pulled in a perfectly normal manner, having a high elastic limit and ultimate strength, and, when finally breaking, showing a smooth face and fibrous structure. The two specimens heated to 1,247° behaved differently. The elastic limit was decidedly lowered, to 21,170 pounds in the case of the slowly cooled bar. When the elastic limit was passed, however, the bars held out remarkably well, the

slowly cooled bar breaking at 53,280 pounds, and the rapidly cooled bar at 58,100 pounds per square inch. After fracture had occurred, it was seen that the surface of these two bars had roughened, having the appearance of a piece of putty when pulled apart. This was much more noticeable, in the case of both bars, upon one side than upon the other, and as the two bars were heated in the furnace together, it may be that the rougher sides were more exposed to oxidizing gases than the other sides which were in contact with each other. To settle this point will require further experimental work. The fractured areas of these two bars showed some bright crystalline spots resembling the grain of overheated carbon steel.

The results of the tensile tests as shown by the table and the curves plotted from it seem to indicate:

1. That there is a fair degree of constancy in the tenacity of the bars heated to below 850° with possibly a slight falling off between 800° and 850°.

2. That at 890° there is a sudden rise in the tensile strength from 56,790 pounds to 59,120 pounds per square inch.

3. That beginning at 900° there is a slight falling off reaching a minimum of 56,690 pounds at 1,000°, from which point it rises again.

4. That at 1,125° the strength reaches a second maximum of 59,000 pounds.

5. That from 1,143° there is a very decided falling off in the strength, reaching 53,280 pounds at 1,247°, beyond which point the experiments were not carried.

The concordance of the results obtained is seen to be quite good, most of the observations lying within 500 pounds of the mean curve. One result only, No. 11, lies widely off, showing a discrepancy of 3,600 pounds. It lies, however, in a portion of the curve where the strength changes rapidly, so a small error in the temperature would make a large apparent error in the strength.

The results of the elastic limit experiments are very similar to those of the ultimate strength, but show much larger variations, and consequently the curve is more doubtful; but it seems to be of the same nature as the ultimate strength curve.

The results of the elongation determinations were very unsatisfactory, owing, as already stated, to the impossibility of matching the ends together. As well as could be determined, however, it seems to show:

FIG. 5. — ETCHED BY POLISHING. SPECIMEN NO. 1. COOLED SLOWLY FROM 647°. TENSILE STRENGTH, 56,660 LBS. × 73.

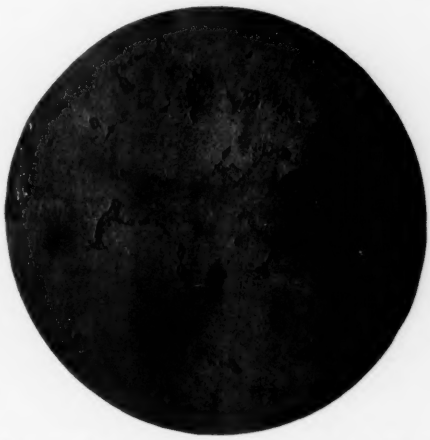

FIG. 6. — ETCHED BY POLISHING. SPECIMEN NO. 20. COOLED SLOWLY FROM 1,247°. TENSILE STRENGTH, 53,230 LBS. × 73.

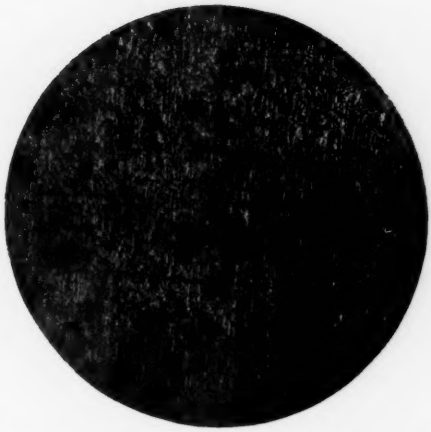

FIG. 7. — ETCHED 30 SECONDS $\frac{1}{10}$ HNO_3. SPECIMEN NO. 3. COOLED SLOWLY FROM 889°. TENSILE STRENGTH, 59,120 LBS. × 73.

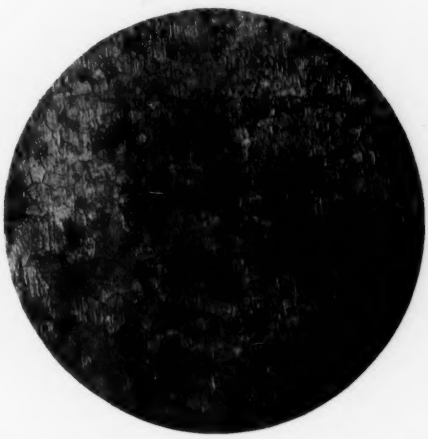

FIG. 8. — ETCHED 30 SECONDS $\frac{1}{10}$ HNO_3. SPECIMEN NO. 7. COOLED SLOWLY FROM 988°. TENSILE STRENGTH, 57,530 LBS. × 73.

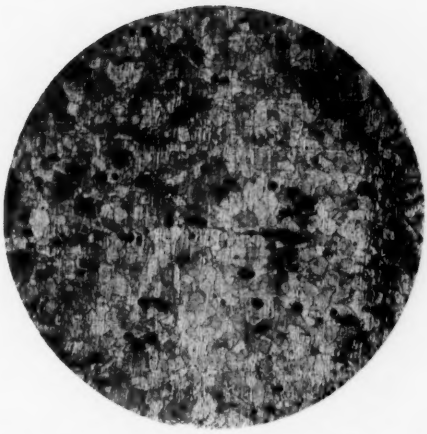

FIG. 9. — ETCHED 30 SECONDS $\frac{1}{10}$ HNO_3. SPECIMEN NO. 28. COOLED SLOWLY FROM 1,041°. TENSILE STRENGTH, 57,190 LBS. × 73.

FIG. 10. — ETCHED 30 SECONDS $\frac{1}{10}$ HNO_3. SPECIMEN NO. 13. COOLED SLOWLY FROM 1,143°. TENSILE STRENGTH, 58,600 LBS. × 73.

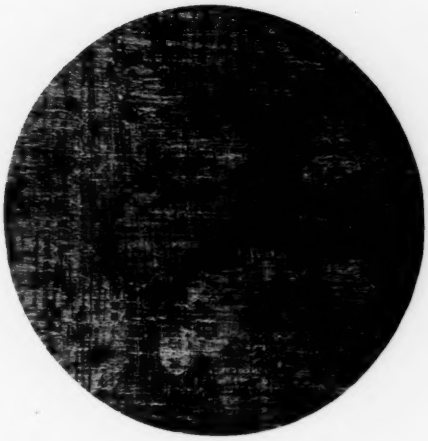

FIG. 11. — ETCHED 30 SECONDS $\frac{1}{10}$ HNO_3. SPECIMEN NO. 20. COOLED SLOWLY FROM 1,247°. TENSILE STRENGTH 53,280 LBS. × 73.

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1. A decrease in elongation to 800°, at which point it is about 29 per cent.

2. A rise to 950°, where it reaches 32.5 per cent.

3. A sudden decrease to 1,000°, at which point it again reaches 29 per cent.

4. A gradual increase up to the limit of the experiments 1,247°, at which temperature the elongation is 31.2 per cent.

The rapidly cooled specimens show a tensile strength quite uniformly from 2,000 pounds to 2,500 pounds higher than the corresponding slowly cooled specimens, with the exception of the 990° rapidly cooled bar which broke at 60,530 pounds, or even higher than the 900° bar. The stretch limit shows a gradual decrease from 43,000 pounds at 695° to 36,000 pounds per square inch at 1,247°. The variations in the elongations seem to be less than the errors of determination.

The microscopic examination of the different specimens has been disappointing. On account of the very small amount of carbon it is extremely difficult, if not impossible, to distinguish the different specimens which have been etched only by polishing in relief. There is in all specimens a ground mass of structurally free ferrite through which are disseminated particles of another constituent which we would expect to be pearlite, but which looks very much more like structurally free cementite, (Figure 5). In no case was it possible to observe the characteristic pearlite markings. The appearance is usually that of an amorphous granular mass which stands in relief. With increase of temperature there is a greater tendency for this constituent to segregate in masses. The scratches which appear on the specimens from polishing would also seem to indicate the presence of cementite, as the course of the scratch is usually interrupted and continues beyond the particle. Figures 5 and 6 show the general appearance of the microstructure of the specimens which have been etched by polishing in relief.

The examination of specimens etched with dilute nitric acid shows that the grain is practically uniform in size in those specimens annealed from 850° and below. When we come to specimen No. 3, Figure 7, slowly cooled from 889°, however, we see a marked change in the structure. The granular structure has disappeared, and has been replaced by a fine close structure resembling porcelain. Specimens Nos. 17, 5, and 9, slowly cooled from 914°, 939°, and 950° respect-

ively, show a fine structure but with grains, visible under a magnification of 84 diameters.

Specimen 7, Figure 8, shows again a larger development. Specimens 12 and 13 show a grain of a size not greatly different, but with a structure very different. Specimen 13, Figure 10, shows parallel striations or bands appearing as alternating dark and light streaks. These bands occur in groups in which the component lines are parallel, but in the different groups they are nearly at right angles. Specimen 20, which was cooled from 1,247° shows an enormous increase in the grain, and also a marked development of these bands or striæ through the grains. This is well shown in Figure 11.

A comparative study of the results of the tensile tests and the microscopic examination show in general a fairly close relation between the size of the grain and the tensile strength. The larger the grain the lower is the tensile strength and elastic limit. The latter seems to be affected by the grain more than the former. The elongation does not show any definite relation to the size of the grain.

The bars which were cooled slowly from below 850°, show a tensile strength of from 55,500 to 56,500 pounds and a grain of fairly large diameter. Passing from 850° to 900° there is a very marked increase in the tensile strength, 59,000 pounds, and an equally sudden diminution in the size of the grains, the latter becoming the finest noted in the series. From 900° to 1,000° the gradual increase in the grain is accompanied by a decrease in the strength, the two being quite proportional.

Above 1,050° there is an increasing size of grain to a slight extent, but the structure here is changing to the banded type. The strength increases through this range to 1,143°, showing that this structure is a strong one, and masks the effects of the grain structure. Above 1,143°, however, the grain increases rapidly and the strength decreases correspondingly.

In general the following tentative conclusions may be drawn :

1. For this particular steel annealing seems to give two points of maximum tenacity and elastic limit, one at 890°, and another at 1,125°. Below 850° the properties of the steel do not change to any appreciable extent, and between 890° and 1,125°, the steel shows a minimum value at 1,000°. Annealing from temperatures above 1,125° causes a decrease in strength with increasing temperature.

The size of the grain is apparently constant or increases but slowly

at temperatures below 850°. At 890° the grain is suddenly refined, and the structure becomes close and almost porcelain-like. From temperatures above this, annealing seems to cause a gradual increase in size slowly up to 1,125°, and rapidly from that point up to the limits of the experiments.

3. Above 1,100° a new type of structure appears which seems to consist of parallel bands and striations sometimes crossing the grain junctions. This type of structure has not, however, been carefully studied, and we are not prepared at present to state its significance.

4. Below 1,000° there is a fairly close relation between the size of the grain and the strength, the latter falling off as the former increases, and *vice versa*. A fine grain indicates a high tensile strength and elastic limit. The latter is affected more than the former.

5. Above 1,000° the banded structure appears to increase the strength, and also somewhat retard the grain development, but at 1,125° the latter takes the ascendency as indicated by the decrease in strength from that point to 1,247°.

The banded structure when not accompanied by an excessive grain appears to be a very strong form.

6. Rapid cooling, as in the open air, gives a higher tensile strength than does slow cooling from the same temperature.

7. The size of the grain of the more rapidly cooled specimens (23–27) follow the same general laws as for the slowly cooled, except that the grain for the same temperature is uniformly smaller.

In connection with the point of maximum tenacity and the related change in structure, it may be said that its position 1,140° corresponds closely with the highest critical point observed by Roberts-Austen in his cooling curve of electro-iron, and also with the point of maximum tenacity observed by Dr. Ball.

It is desired to express the thanks of the authors to Mr. C. L. Norton, without whose aid and kindly advice much of the work would have been impossible; likewise to Professors Miller and Schwamb for the use of much valuable apparatus.

PERMANENT STANDARDS FOR USE IN THE ANALYSIS OF WATER.

By DANIEL D. JACKSON.

COLORIMETRY plays such an important part in the analysis of water that standards for comparison are in constant use, and in laboratories for water analysis much time is consumed in the preparation of these standards. At the present writing permanent standards are used for the determinations of color, turbidity, and nitrate. It is proposed to add to this list permanent standards for the determination of ammonia, nitrite, and iron, all of which have been determined heretofore by the use of comparisons made from a series of known amounts of the constituent to be determined, and none of which standards are sufficiently permanent to be used more than once. It may be well to describe the permanent standards already employed, and then to take up in detail the new standards proposed.

COLOR.

An instrument which has been in common use for the estimation of the color of water in England, is the Tidy Colorimeter.[1] This consists of two 2-foot tubes with ground glass ends. The water to be examined is placed in one of these tubes, and in the other is poured distilled water. Two wedges, one containing potassium bichromate for the yellow color, and one containing copper sulphate for the blue color, are used. When the superimposed wedges examined through the tube of distilled water exactly equal the color of the water to be determined, the results are expressed as read upon the wedges in amounts of yellow and blue.

In America the determination of the color of water has been based upon the standard recommended by Leeds,[2] — that of Nesslerized ammonia, and all results have been reported in terms of this standard or of some scale based directly or indirectly upon it.

[1] Crookes, Odling & Tidy. Chem. News, 43, 174. Am. Chem. Jour., 14, 300.

[2] Proc. Am. Chem. Soc., 2, 8.

The natural water standards are made by a series of dilutions of a highly colored surface water which are compared with the Nessler scale or with the Lovibond tintometer.[1] The Nessler scale and standards based directly upon it are not uniform in the low portion of the scale, chiefly because the amount of Nessler solution added to the ammonia standards is a large factor in the production of color. What should be a standard of .10 is in reality .18, and the extra .08 is due for the most part to the color of the two cubic centimeters of Nessler solution added. In the upper part of the scale this color of the Nessler solution itself sinks into insignificance. But inasmuch as the lower part of the scale is constantly used in water analysis, it is necessary that it should be uniform.

Hazen's[2] platinum-cobalt color standard is designed to fulfill this purpose. It is prepared as follows: 1.246 grams of potassium platinic chloride ($PtCl_4.2KCl$) and 1 gram of cobaltous chloride ($CoCl_2.6H_2O$) are dissolved in distilled water, 100 c.c. of strong hydrochloric acid added, and the solution made up to 1,000 c.c. with distilled water. If we express the results in parts per million of platinum, this solution is a standard of 500, and standards made by diluting 1, 2, and 3 c.c. of this solution in 50 c.c. Nessler tubes give colors of 10, 20, and 30. Better tubes for this purpose are 100 c.c. tubes of colorless glass 2.2 cm. ($\frac{7}{8}''$) in diameter, and 23.5 cm. ($9\frac{1}{4}''$) to the 100 c.c. mark. A series of twelve tubes are prepared by adding the following amounts of the standard to the tubes and making up to the 100 c.c. mark with distilled water.

Amount of strong standard added.	Standard color. (Pts. per million platinum.)
0 c.c.	0
1 c.c.	5
2 c.c.	10
3 c.c.	15
4 c.c.	20
5 c.c.	25
6 c.c.	30
7 c.c.	35
8 c.c.	40
10 c.c.	50
12 c.c.	60
14 c.c.	70

[1] E. H. Richards and J. W. Ellms, Jour. Am. Chem. Soc., XVII, January, 1896.

[2] Am. Chem. Jour., XIV, No. 4.

Standards beyond this point are difficult of comparison, and waters of deeper color should be read by dilution. The reason for this difficulty is that the components of the color in the natural water are not the same as in the platinum-cobalt standard, and if the depth of the liquid remains the same, the relative absorption of light by these components varies with the strength of the color. The following diagram, Figure 1, illustrates this point:

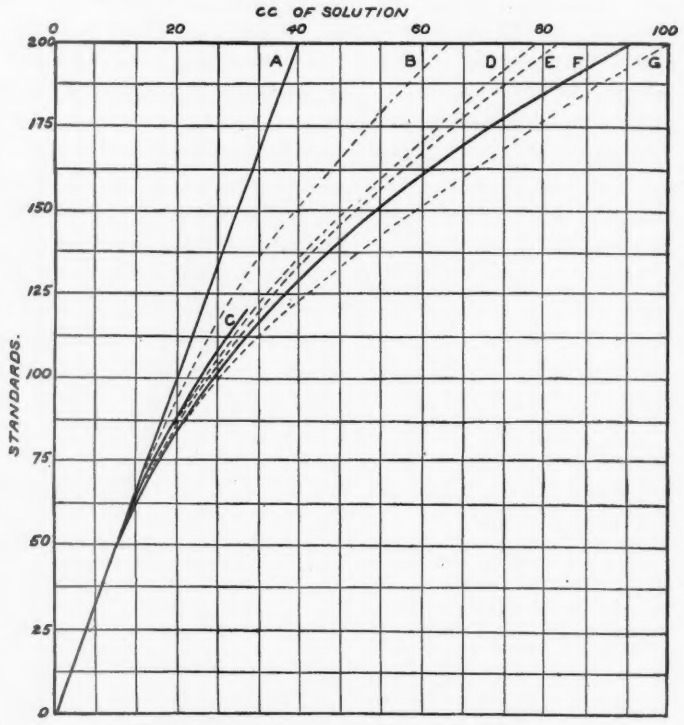

FIG. 1. — COMPARISON OF COLOR STANDARDS.
Figures at left = parts per million of platinum.

Line *A* represents the cubic centimeters of Hazen's standard necessary to make the standards figured at the left if made up in the 100 c.c. tubes described. In this case the cubic centimeters of platinum and of cobalt used are the same. The other lines represent the excess of cobalt solution of the same strength required to match various colored waters, both artificial and natural.

B = Maple leaf extract.
C = Natural water standard from Fall River, Massachusetts.
D = Cedar leaf extract.
E = Birch leaf extract.
F = Natural water standard from Westboro, Massachusetts.
G = Natural water from Winooski, Vermont.

Since this diagram was made, a leaf extract and a natural surface water have been examined which follow Hazen's standard (line *A*) to 150, and then fall off toward the red (line *B*). The hue of both of these waters was inclined toward the green.

The conclusions to be drawn from this diagram and from the foregoing considerations are:

(1) That if the highly colored waters were uniform in hue, it would be feasible to make standards from two separate solutions of platinum and cobalt to correspond with the diagram, but that it is impossible to make a set of standards which would always match the color of surface waters because of the difference in hue in various waters, and even in the same water at different seasons of the year.

(2) That while the natural water standards follow more closely the hue usually found in colored waters, they do not agree with each other in hue if the source of collection is different.

(3) That this failure to agree in hue takes place at about the same point on the scale whether the platinum-cobalt standards or the natural water standards be used.

(4) That above a standard of 70 parts per million of platinum on Hazen's scale, or .90 on the Nessler scale, the color of a water should be read by dilution even when natural water standards are employed.

(5) That Hazen's platinum-cobalt standard if read below 70 is perfectly uniform, and the most practical and accurate standard for the determination of the color in water.

Turbidity.

Professor Mason's[1] permanent standards for turbidity are made by adding a weighed amount of kaolin to distilled water. A series of standards are then prepared which are graduated in parts per million of kaolin. On account of the variation in the size of the particles in kaolin, and the great differences found in different kaolins, it has been

[1] Examination of Water, page 12. John Wiley & Sons.

deemed advisable to use finely powdered diatomaceous earth[1] instead of kaolin. The diatom frustules being finely striated, break up when ground into particles of great uniformity in size, and are composed of practically pure silica unacted on by water or acids.

This diatomaceous earth is ignited to free it from organic matter, ground to an impalpable powder, put through a 200-mesh sieve to break up the lumps produced in grinding, dried at 100° C., cooled in a desiccator and kept in a tightly stoppered bottle. One gram of this earth is weighed out and put into 1 liter of distilled water. This mixture equals a standard of 1,000. Twelve dilute standards are prepared in 100 c.c. tubes like those described for color standards, and made up to the 100 c.c. mark in the following manner:

Amount of strong standard added.	Standard turbidity. (Pts. per million silica.)
.0 c.c.	0
1.0 c.c.	10
1.5 c.c.	15
2.0 c.c.	20
2.5 c.c.	25
3.0 c.c.	30
4.0 c.c.	40
5.0 c.c.	50
6.0 c.c.	60
7.0 c.c.	70
8.0 c.c.	80
9.0 c.c.	90
10.0 c.c.	100

These standards are kept tightly corked and are shaken violently before comparison with the water to be measured for turbidity. When new corks are used they are boiled in distilled water several times to extract any coloring matter which they may contain. For higher turbidities the water to be examined is diluted until it falls within the standard scale. The turbidity is always compared sidewise toward the light. For the reading of low turbidities in water, similar sets of permanent standards are prepared in bottles of the same size as those employed for collection of the samples of water. Turbidities between 0 and 20 have been found to be determined much more accurately by the use of these bottles.

[1] G. C. Whipple and D. D. Jackson, *Technology Quarterly*, Vol. XII, No. 4; also *Technology Quarterly*, Vol. XIII, No. 3.

Nitrogen as Nitrate.

A most satisfactory permanent standard for nitrate as determined by the phenol-sulphonic acid method is made up by Mason as follows:

Strong standard nitrate solution is made by dissolving .72 gram of pure potassium nitrate in 1 liter of distilled water.

Dilute standard nitrate is then made from the strong solution by evaporating 10 c.c. of the strong solution just to dryness and then adding 2 c.c. of phenol-sulphonic acid, rubbing the residue quickly and thoroughly with the acid by means of a glass rod, and making up to 1 liter with distilled water.

Permanent standards for comparison are made from this dilute solution in 100 c.c. tubes, 3 cm. ($1\frac{1}{8}''$) in diameter, and 13.2 cm. ($5\frac{1}{4}''$) to the 100 c.c. mark. Five cubic centimeters of strong ammonia is added to each tube, and the series of standards made up as follows:

Amount of dilute standard added.	Standard nitrate.
.0 c.c.	.0
1.0 c.c.	.1
3.0 c.c.	.3
5.0 c.c.	.5
7.0 c.c.	.7
10.0 c.c.	1.0
15.0 c.c.	1.5
20.0 c.c.	2.0
25.0 c.c.	2.5
30.0 c.c.	3.0
35.0 c.c.	3.5
40.0 c.c.	4.0

If the water to be examined is very low in nitrate, 50 c.c. are evaporated to dryness; 25 c.c. is the usual amount taken, but if the water is high in nitrate less should be used. The residue is then treated with 1 c.c. of phenol-sulphonic acid and thoroughly covered with the acid by stirring with a glass rod. A small amount of distilled water is then added (7–10 c.c.), after which it is rendered alkaline with ammonia. The solution is now washed into a 100 c.c. tube, made up to the mark with distilled water, and the yellow color produced is compared with the permanent standards. If, for example, 50 c.c. of the water is taken, then the figure obtained by comparison with the standards is multiplied by .2 to obtain parts per million of nitrogen as nitrate.

If the standards are kept well corked with stoppers which have had the coloring matter extracted from them by boiling water, they will keep perfectly well for several months. Consequently artificial standards are in this case entirely unnecessary.

Nitrogen as Free and Albuminoid Ammonia.

The success of Hazen's platinum-cobalt standard for color has led the author to construct tables for the preparation of similar permanent standards for use in the colorimetric determinations of ammonia, nitrite and iron.

The standards which are made up for the determination of ammonia may be duplicated by a permanent set prepared from potassium platinic chloride and cobaltous chloride, and with a little practice the Nessler solution may be prepared to exactly fit the standards each time.

Preparation of Nessler Solution. — Dissolve 61.75 grams of potassium iodide in 250 c.c. of redistilled water, and add a cold solution of mercuric chloride which has been saturated by boiling with excess of the salt. Pour in the mercury solution cautiously, and add an amount just sufficient to make the color a permanent bright red. With a little practice the exact depth of color can be easily duplicated. It will take a little over 400 c.c. of the mercuric chloride solution to reach this end point. Dissolve the red precipitate by adding exactly .75 gram of powdered potassium iodide. Then add 150 grams of potassium hydrate dissolved in 250 c.c. of water. Make up to 1 liter. Mix thoroughly and allow the precipitate formed to settle.

It is best to make up a large amount of Nessler solution, and if by its use the ammonia standards do not fit the artificial ones prepared from the platinum and cobalt solutions, a little more mercuric chloride to increase sensitiveness, or potassium iodide to decrease it, will bring the Nessler solution to the point where, if just 2 c.c. are used, the regular ammonia standards will exactly fit the artificial ones. The artificial standards may then be employed for the ammonia readings until the Nessler solution tested is entirely used up. Of course, each new lot of Nessler solution should be compared to see that it has the proper degree of sensitiveness to fit the standards. Very close to 2 c.c. of Nessler solution should always be used in Nesslerizing, as the amount of this solution effects the depth of color, especially in the

lower part of the scale. To prepare the permanent standards two separate solutions are necessary.

Platinum Solution. — Weigh out 2 grams of potassium platinic chloride ($Pt\ Cl_4.2\ KCl$), dissolve in a small amount of water; add 100 c.c. of strong hydrochloric acid, and make up to 1 liter.

Cobalt Solution. — Weigh out 12 grams of cobaltous chloride ($CoCl_2.6\ H_2O$), dissolve in distilled water; add 100 c.c. of strong hydrochloric acid, and make up to 1 liter.

Varying amounts of these two solutions are required, because the color of the Nessler standards becomes more and more reddish as the amount of ammonia increases. The standards are made up in 50 c.c. Nessler tubes 1.7 cm. ($\frac{1}{16}''$) in diameter, and 21 cm. ($8\frac{1}{4}''$) from the bottom to the 50 c.c. mark. Twelve standards are prepared by filling up to the 50 c.c. mark with distilled water as follows:

c.c. Pt. solution.		c.c. Co. solution.		Standard Ammonia.
1.0	+	.0	=	.0
1.8	+	.0	=	.1
3.2	+	.0	=	.3
4.5	+	.1	=	.5
5.9	+	.2	=	.7
7.7	+	.5	=	1.0
9.4	+	.9	=	1.3
10.4	+	1.3	=	1.5
12.7	+	2.2	=	2.0
15.0	+	3.3	=	2.5
17 3	+	4.5	=	3.0
19.0	+	5.7	=	3.5
19.7	+	7.1	=	4.0
19.9	+	8.7	=	4.5
20.0	+	10.4	=	5.0
20.0	+	15.0	=	6.0

The following diagram, Figure 2, expresses in an interesting way the relation between the standards and the two solutions used:

It will be seen that very little cobalt is required until the point .7 is reached. Then the cobalt required increases rapidly. It is at about this same point in the Hazen color standards that difficulty in matching begins, because the deeper colored waters appear more reddish than the standards. But as before stated, in Hazen's color standards the color usually read is so low that standards made from two separate solutions are neither practical nor necessary.

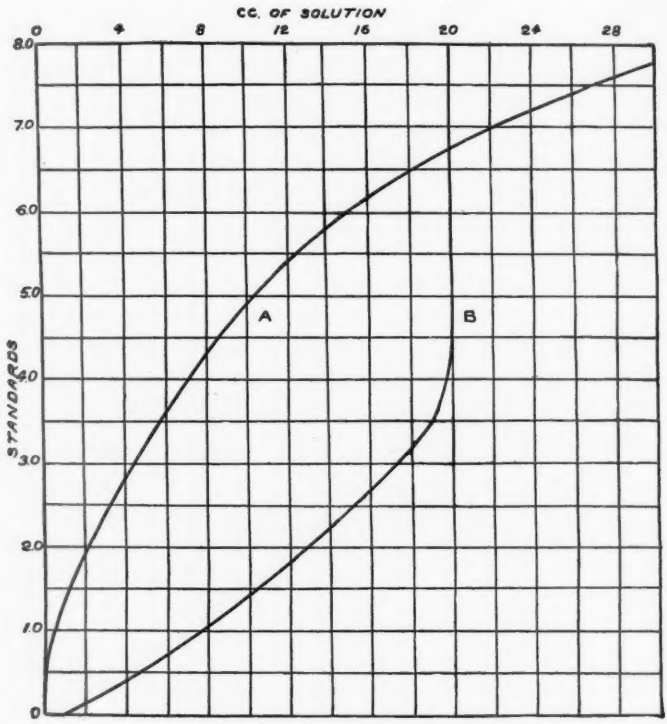

FIG. 2. — PERMANENT AMMONIA STANDARDS.
A, Cobalt Solution. *B*, Platinum Solution.

The components of the colors in the natural and in the artificial ammonia standards have not the same appearance at different concentrations, and the same depth. This fact may be easily demonstrated by holding the standard of 6.0 sidewise toward the light together with the regular Nessler ammonia standard. While they agree perfectly on examining them lengthwise through the tubes, they do not agree at all sidewise where slight depth is exposed. In this position the artificial standard is decidedly pink, and not brownish yellow as it appears lengthwise. This difference in the coefficient of absorption of light renders it impossible to make standards for ammonia from any one single platinum-cobalt solution.

In the ammonia determination the water is distilled into 50 c.c. tubes, and after the ammonia tubes to be examined have come to room

temperature they may be Nesslerized. They should be kept for five or six minutes until the full depth of color is reached. Then they may be read at leisure, as no further change takes place in them for several hours. The temperature of the waters to be read may vary between 18° and 25° C. (64° and 77° F.) without material change in depth of color. If, for example, 500 c.c. of water is distilled and the sum of the ammonia tubes, either free or albuminoid, compared with the standards, reads 4.2, then the water contains .084 parts per million of nitrogen as ammonia.

Nitrogen as Nitrite.

Standards made from two separate solutions are best in this case also.

Cobalt Solution. — Weigh out 24 grams of cobaltous chloride ($CoCl_2.6H_2O$) and dissolve it in distilled water. Add 100 c.c. of strong hydrochloric acid, and make up to 1 liter with distilled water.

Copper Solution. — Weigh out 12 grams of dry cupric chloride ($CuCl_2.2H_2O$); dissolve in water; add 100 c.c. strong hydrochloric acid and make up to 1 liter with distilled water.

The standards are made up in 100 tubes like those described for nitrate standards. The following table gives the proportions of each solution to be made up to the 100 c.c. mark:

c.c. Cobalt solution.	c.c. Copper solution.	Standard nitrite.
.0	.0	0
1.1	1.1	1
3.5	3.0	3
6.0	5.0	5
12.5	8.0	10
20.0	8.0	15

The standard of 15, although it can be compared with the nitrite in color, still is not so satisfactory as the others, due to the increased effect of the yellow component either in the copper or the cobalt solution. This it seems, however, cannot in any way be obviated.

To determine nitrite fill a 100 c.c. Nessler tube with water to be tested, add 1 c.c. of hydrochloric acid (1 : 4), then 2 c.c. of sulphanilic acid (8 grams per liter), and finally 2 c.c. of naphthylamine hydrochlorate (8 grams per liter with 10 c.c. of strong hydrochloric acid), allow to stand twenty minutes until the full development of the color appears.

The tubes should be tightly corked, as nitrite is often rapidly absorbed from the air. The temperature unless nearly at the freezing point does not effect the development of the color. If 100 c.c. of water is taken, and on treatment it develops a color corresponding to the standard of 3, then the water contains .003 parts per million of nitrogen as nitrite. The following diagram, Figure 3, shows the proportion of the two solutions used.

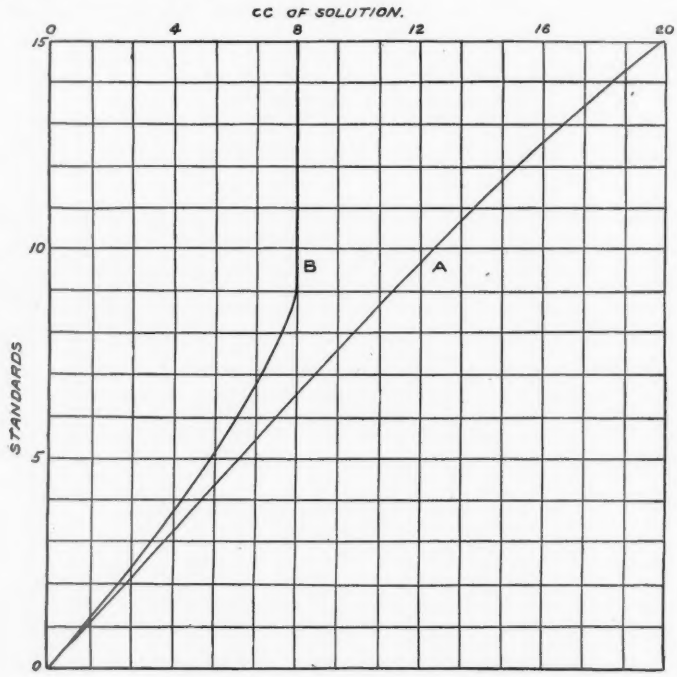

FIG. 3. — PERMANENT NITRITE STANDARDS.
A, Cobalt Solution. *B*, Copper Solution.

IRON.

Very satisfactory standards for the iron determination may be prepared from platinum and cobalt, but in this case also, the standards must be made from two separate solutions.

Platinum Solution. — Weigh out 12 grams of potassium platinic chloride, dissolve in distilled water, add 100 c.c. of strong hydrochloric acid and make up to 1 liter with distilled water.

Cobalt Solution. — Weigh out 24 grams of dry cobaltous chloride crystals, dissolve in a small amount of water, add 100 c.c. of strong hydrochloric acid and make up to 1 liter with distilled water.

The standards are prepared in 100 c.c. tubes like those used for nitrate standards, and are made up to the 100 c.c. mark with distilled water in the proportions given below:

c.c. Cobalt solution.		c.c. Platinum solution.		Standard iron.
.0	+	0	=	.0
1.0	+	2	=	.1
3.0	+	6	=	.3
5.0	+	10	=	.5
7.5	+	14	=	.7
11.0	+	20	=	1.0
17.0	+	28	=	1.5
24.0	+	35	=	2.0
32.0	+	39	=	2.5
43.0	+	40	=	3.0
55 0	+	40	=	3.5
67.0	+	40	=	4.0

The following diagram, Figure 4, is interesting as showing the relation of the components used, and the impossibility of matching the higher colors by a single solution.

The brownish red color produced in the determination of iron is unaffected by ordinary variations in temperature. As the color begins to fade soon after it is developed, it is necessary to make the comparisons directly after adding the potassium sulphocyanide solution.

Inasmuch as the amount of each reagent used affects the depth of color obtained in the iron determination, it is necessary to follow very carefully the directions given below.

A known quantity of the water to be tested should be evaporated to dryness, and *the organic matter destroyed by ignition.* The residue is then treated with 5 c.c. of hydrochloric acid (1 : 1) and heated carefully over a free flame, so that boiling takes place for an instant. The liquid is then washed into a 100 c.c. tube and made up to the 100 c.c. mark with distilled water. Two or three small drops of potassium permanganate solution (5 grams per liter) are added, and the tube is allowed to stand a few minutes. If the red color disappears, add two or three more drops of permanganate solution, and repeat this

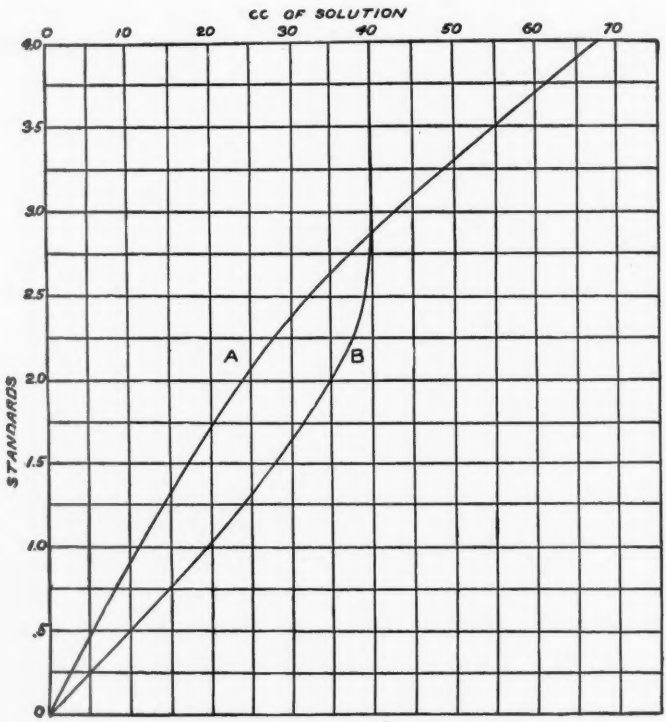

FIG. 4. — PERMANENT IRON STANDARDS.
A, Cobalt Solution. *B*, Platinum Solution.

until the color becomes permanent and all ferrous iron has been oxidized; 10 c.c. of potassium sulphocyanide (20 grams per liter) are then added, and the liquid thoroughly mixed by pouring from one tube into another. If, for example, 100 c.c. of water is taken for evaporation, the figure found by comparison with the standards equals directly parts per million of iron.

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THE EFFECT OF TEMPERATURE, OF COLLOIDAL FERRIC HYDRATE, AND OF A MAGNETIC FIELD ON THE HYDROLYSIS OF FERRIC CHLORIDE.[1]

By H. M. GOODWIN and FREDERICK W. GROVER.

The present investigation is a continuation of one published by one of us[2] in 1896, on the changes which take place in a neutral ferric chloride solution when greatly diluted. Such solutions when first prepared of a concentration of about 0.001 normal are nearly colorless but rapidly change to a deep reddish brown, and this gradual color reaction is accompanied by a corresponding increase in the electrical conductivity of the solution. In the paper cited, the hydrolytic reaction giving rise to this phenomena was studied by following the changes in the conductivity of the solution, and the main results of the investigation may be summarized as follows:

1. The electrical conductivity of dilute ferric chloride solutions increases with the time.

2. The rate of increase increases very rapidly with the dilution.

3. The increase in conductivity does not begin at once on dilution, but only after the lapse of a certain time.

4. This initial lag or time required to start the reaction increases rapidly with the concentration, being for example, 1 minute for a 0.0006 normal solution, 15 minutes for a 0.0012 normal solution, and 45 minutes for a 0.0024 normal solution.

5. The time required for a solution to reach a state of equilibrium increases enormously with the dilution, a 0.0001 normal solution requiring, for example, only 3 hours, while a solution six times as strong requires over a week.

6. The hydrolytic dissociation was computed and found to be very large in dilute solutions.

The explanation offered for this peculiar behavior was the gradual

[1] Reprinted from the Physical Review, Vol. 9, No. 4, October, 1900.

[2] Goodwin, Phys. Rev., 9, 251, 1896. *Technology Quarterly*, 9, 254, 1896.

formation of Graham's colloidal ferric hydrate from the electrolytically hydrolized ferric chloride, according to the reaction

$$x\,\overset{+}{\mathrm{Fe}}\overset{+}{\mathrm{OH}} + x\,2\bar{\mathrm{O}}\mathrm{H} = (\mathrm{FeO_3H_3})\,x.$$

The formation of colloidal hydrate accounted for the color changes observed, while the removal of the $\overset{+}{\mathrm{Fe}}\overset{+}{\mathrm{OH}}$ ions from the solution displaced the hydrolytic equilibrium, thus causing more chloride to be hydrolyzed with accompanying increase of conductivity. The initial lag observed in the reaction, and the remarkable acceleration of its rate when once started was explained on the hypothesis that the rate of formation of the colloidal hydrate was dependent on the presence of a certain amount of the colloid itself, analogous to the rate of crystallization being a function of the number of crystallizing nuclei, around which the crystals can form.

The present investigation was undertaken first to study the effect of temperature on the rate of the reaction, the former measurements all having been made at 25°; second, to test the above hypothesis regarding the cause of the accelerated rate of the reaction after the lapse of a certain time; and third, to see if any effect could be observed on the rate of the reaction of a strong magnetic field.

Apparatus and Method.

The conductivity measurements were made by the familiar Kohlrausch method. The solutions were diluted as in the previous investigation by adding with a pipette a few cubic centimeters of a strong solution of neutral ferric chloride to a previously weighed amount of distilled water brought to the proper temperature of the experiment. This water was contained in 250 c.c or 500 c.c. thoroughly steamed wide-necked glass bottles which served also as measuring cells. It was found very advantageous to use "plunge electrodes" in cells of this kind (Kohlrausch & Holborn's Leitvermögen der Electrolyte, p. 19) instead of the usual Arrhenius type previously employed. The considerable care and patience required in the preparation of these electrodes was more than compensated for by their absolute constancy, and particularly the independence of their "constant" from the position of the electrodes in the bottle. Electrodes about one square centimeter in area platinized with a Lummer-Kurlbaum solution gave

an excellent minimum for most dilutions investigated. The solutions were investigated at 0°, 15°, and 25° C. The first temperature could of course be maintained indefinitely constant by a large ice bath packed in hair felt in which the bottles were completely immersed. A temperature of 15° C. was maintained constant to within 0.1° during the day, and 0.2°–0.3° during the night by means of a large tank of water, insulated from outside temperature changes by being packed in a box with 6 inches of finely divided cork, and covered with 4 inches of hair felt. A temperature of 25° was maintained indefinitely constant to a few hundredths of a degree in the large 5 x 3 x 3 foot automatically regulated and electrically heated thermostat of the laboratory.

Solutions.

Ferric Chloride. — The stock ferric chloride solution used in the following experiments was made from a preparation of sublimed ferric chloride from Eimer and Amend. A quantity weighed from a weighing tube was made up to 1 gram-equivalent in a liter and then analyzed for chlorine. Three analyses gave an equivalent normality of 0.996, 1.001, and 0.999, the mean being 0.9987. This solution had an equivalent conductivity of 43.6 at 24.96° C. after standing about a week. This stock solution was then diluted ten or a hundred times for the secondary stock solutions used in the subsequent great solutions.

Graham's Colloidal Ferric Hydrate. — A solution of Graham's soluble colloidal hydrate was prepared by treating a saturated solution of pure (unsublimed) ferric chloride with ammonium carbonate with constant stirring, until the light colored precipitate which formed just refused to dissolve on further stirring. The color of the solution rapidly turned to an intense garnet color. It was then subjected to dialysis for 32 days. The concentration of the resulting solution was determined by evaporating to dryness and igniting portions of 10 c.c. each, and weighing the ferric oxide. The mean of two determinations showed it to be 0.3085-equivalent normal with respect to $Fe(OH)_3$. It still contained some ammonium salts as shown by a slight visible volatilization on first heating, and from the fact that the solution had a considerable conductivity which, had it contained only colloidal hydrate, should not be the case. At 18.1° its specific conductivity was 0.00304, which corresponds to that of an ammonium chloride solution about 0.02 normal.

Experimental Results.

In the following tables are tabulated the results obtained at 25°, 15.5°, and 0°, with solutions of the indicated concentrations, C always being expressed in *gram equivalents* in a liter. The conductivities are those observed at the indicated time intervals elapsing from the time of dilution. The values are expressed as equivalent conductivities in reciprocal Siemen's units for convenience of comparison with former measurements.

TABLE I.

$C = 0.000150$. $t = 24.92°$. Diluted from $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 40	295.3	37 25	363.6
2 35	310.2	58 50	364.8
4 25	323.1	1 28 45	366.9
6 15	326.8	2 1 15	366.9
7 30	328.3	.....	.....
14 35	350.9	20 19	364.8
18 35	353 0	21 21	364.8
27 35	358.7	.....	.....

TABLE II.

$C = 0.0004545$. $t = 25.12°$. Diluted from $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 0	260.2	13 10	319.8
2 30	267.8	14 45	322.1
3 0	272.5	18 10	326.8
3 45	280.3	21 45	330.2
4 20	284.9	27 40	333.8
4 50	287.8	33 40	335.6
5 30	295.7	37 35	338 6
6 0	297 9	1 42 0	351.1
6 35	300 6	2 10 0	352.4
7 5	302.2	4 50 0	352.4
8 30	306 6	.....	.....
10 40	315.5	27	351.
12 15	318.7	.....	.....

TABLE III.

$C = 0.000906$. $t = 25.09°$. Diluted from $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 40	214.6	12 30	277.0
3 20	223.5	15 0	283.3
3 55	229.1	21 0	294.8
4 40	236.8	24 30	300.1
5 30	242.5	32 15	309.3
1 20	252.2	45 30	318.7
6 50	255.6	59 30	326.4
7 40	259.4	1 15 30	331.7
8 20	263.0	1 39 30	337.7
9 40	266.8	2 51 0	344.6
10 30	270.7	.....	.....
11 0	272.4	.....	.....
12 0	275.4	.....	.....

TABLE IV.

$C = 0.001335$. $t = 25.04°$. Diluted from $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 0	200.6	23 45	274.2
2 55	209.1	27 45	279.9
3 25	212.6	44 0	294.0
4 25	222.9	50 0	297.7
5 15	228.7	1 30 0	316.6
6 45	234.5	2 6 0	325.1
9 45	246.3	2 24 0	328.1
14 30	259.2	2 35 0	329.6
17 5	266.3	.....	.....

TABLE V.

$C = 0.00360$. $t = 24.96°$. Diluted from $C = 0.999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 45	183.5	41 20	212.3
4 20	185.3	56 0	222.2
5 0	185.3	1 9 0	229.7
7 55	186.9	1 26 20	239.3
8 45	187.6	1 38 0	243.0
10 10	188.2	1 51 0	248.0
13 0	190.3	2 11 0	254.5
16 0	193.2	2 36 0	261.6
23 15	198.7	2 49 0	264.5
26 25	201.1	2 58 0	266.4
34 45	207.4	3 3	268.1

TABLE VI.

$C = 0.00750$. $t = 24.87°$. Diluted from $C = 0.999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
4 0	171.9	42	176.0
8 0	172.8	56	178.0
11 30	172.8	1 2	180.2
15 0	173.4	3 7	206.7
17 0	173.2	3 9	207.5
20 0	173.7	3 14	208.9
23 0	174.6	3 20	210.0
27 0	174.3	.....	.....
30 0	175.6	21	260.
35 0	175.3	.....	.....

TABLE VII.

$C = 0.000150$. $t = 15.5°$. Diluted from $C = 0.0100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
3 15	249.3	18 20	281.7
4 15	255.3	19 45	283.6
5 0	259.0	26 10	287.1
6 45	264.1	51 0	292.8
8 50	269.6	1 1 0	294.7
10 10	273.7	1 31 0	296.5
11 40	274.8	2 6 0	297.7
12 10	276.0	.....	.....
14 10	279.3	18 23	301.6

TABLE VIII.

$C = 0.00033$. $t = 15.4°$. Diluted from $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 35	207.4	22 0	256.2
3 30	210.2	31 30	260.3
5 5	220.8	38 10	263.2
6 50	231.8	49 50	267.6
7 30	233.8	1 0 35	269.4
9 20	238.6	1 27 50	274.7
12 35	245.0	2 9 10	279.1
14 10	246.8	.....	.....
17 50	251.4	25 54	286.0

TABLE IX.

$C = 0.0004545$. $t = 15.9°$. Diluted from $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
3 40	182.2	25 40	233.3
4 25	186.6	31 0	238.7
5 20	191.1	1 0 35	256.1
6 40	197.2	1 19 20	262.0
7 55	201.5	1 38 0	268.3
10 25	209 4	1 49 0	270.9
13 55	217 4	1 55 0	272.2
16 40	221.9	.....	.....
21 35	228.7	19 28	301.9

TABLE X.

$C = 0.000909$. $t = 15.7°$. Diluted from $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 15	167.0	54 0	206.2
2 50	167 5	1 9 0	214.1
3 15	168 2	1 29 0	222.1
3 45	168 3	1 39 0	225.6
4 15	168.7	1 57 0	231.5
5 30	169.6	2 28 0	238.9
6 0	170.0	2 47 0	243.0
7 45	170.9	3 24 0	249.9
14 30	177.1	23	298.3
25 45	187.1	.....	.....
38 15	196.5	5 d. 23 h.	299.5

TABLE XI.

$C = 0.001335$. $t = 15.5°$. Diluted from $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 0	167.8	1 13	188.6
2 50	168.0	1 43	203 3
5 35	168.9	2 13	212 4
10 10	170.0	2 52	222.4
14 20	170 8	22 49	285.9
27 50	175.8	.....	.....
38 30	179.7	7 d. 20 h.	300.7

TABLE XII.

$C = 0.00500$. $t = 15.6°$. Diluted from $C = 0.999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
7	146.4	2 38	149.0
10	146.5	2 53	149.3
18	146.6	3 6	149.1
28	147.0	8 10	153.1
32	147.1	1 2 22	198.0
41	147.2	3 5 48	219.3
57	147.3	4 5 32	223.1
1 28	147.8	6 4	223.4

Solution colorless during first 8 hours.
Solution deep yellow after 1 day.

TABLE XIII.

$C = 0.00750$. $t = 15.5°$. Diluted from $C = 0.999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
4	139.5	21 58	140.0
1 41	140.8	3 1 51	178.1
1 52	140.8	4 0 59	188.9
2 3	141.0	6 0 31	199.1
4 2	140.4	.....	.....

Solution colorless during first 21 hours.
Solution deep yellow after 3 days.
Solution slightly turbid after 4 days.
Solution very turbid after 6 days.

TABLE XIV.

$C = 0.000150$. $t = 0°$. Diluted from $C = 0.00999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
4 0	122.6	3 11	171.7
6 30	129.1	4 14	174.6
8 0	131.1	6 4	178.4
10 0	135.0	6 54	178.9
14 40	140.5	7 28	179.8
26 0	145.4	24 44	183.0
1 24 0	162.8	3 d. 2 h.	183.0
2 37 0	170.6	.....	.....

TABLE XV.

$C = 0.00033$. $t = 0°$. Diluted from $C = 0.00999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 30	121.1	34 30	124.6
3 15	121.6	56 0	127.6
5 20	121.7	1 16 0	131.1
6 30	122.1	1 50 0	136.6
9 0	122.1	2 34 0	142.5
11 10	122.6	3 1 0	145.4
17 0	123.2	1 d. 20 h.	194.1
25 15	124.6	3 d. 40 m.	200.1

TABLE XVI.

$C = 0.0004545$. $t = 0°$. Diluted from $C = 0.090$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
6 0	113.9	6 8	130.8
7 0	114.3	6 53	135.5
7 30	114.7	7 10	137.0
9 0	115.3	7 36	138.4
12 0	116.1	d. h. m.	.....
23 0	117.3	1 3 30	167.6
1 26 0	123.2	1 4 14	168.6
3 11	121.1	1 6 13	169.5
4 4	125.9	.....	.....

TABLE XVII.

$C = 0.000909$. $t = 0°$. Diluted from $C = 0.0999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
6	113.1	1 40	113.9
25	112.0	2 20	115.0
31	112.1	3 16	116.1
51	112.6	1 5 20	143.3

$C = 0.000909$. Diluted from $C = 0.0909$.

37	110.0	1 6 30	144.5
2 54	113.0	4 1 40	160.0
6 19	113.3	5 1 28	159.9
22 23	114.2	.....	.....

TABLE XVIII.

$C = 0.001335$. $t = 0°$. Diluted from $C = 0.0999$.

Time elapsed. d.	h.	m.	Equivalent conductivity.	Time elapsed. d.	h.	m.	Equivalent conductivity.
		27	107.9	1	19	11	123.4
	1	24	107.9	2	2	7	130.0
	1	54	107.9	2	19	13	136.0
1	1	15	107.8	4	19	6	145.1
1	17	32	121.3	8	2	32	147.6

Solution deep yellow.

TABLE XIX.

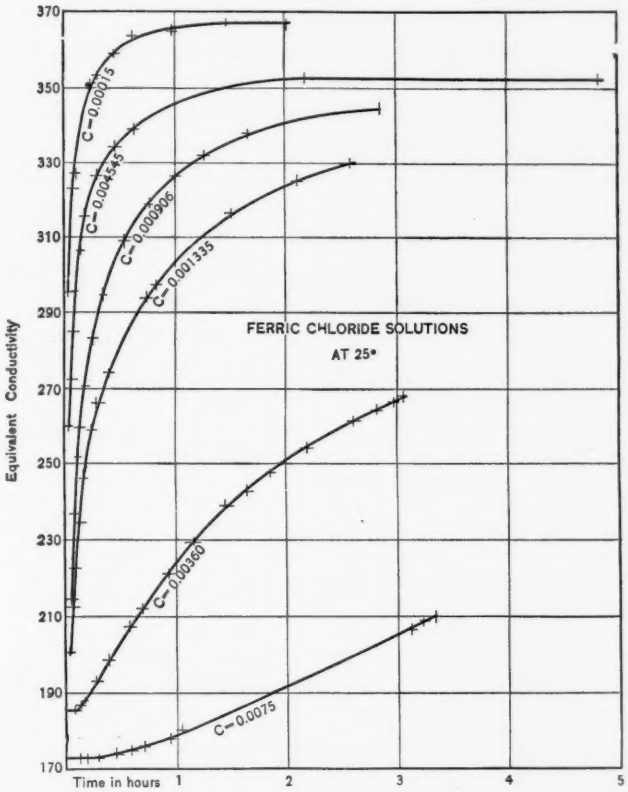
$C = 0.00250$. $t = 0°$. Diluted from $C = 0.0999$.

Time elapsed. d.	h.	m.	Equivalent conductivity.	Time elapsed. d.	h.	m.	Equivalent conductivity.
		32	101.4	5	1	23	106.7
2	0		99.9	6	1	53	112.6
3	1	19	99.7	6	21	18	117.8
3	22	20	101.2	10	—		125.1
4	20	27	105.6	12	—		128 5

Discussion of Results.

The data in the preceding tables is represented graphically in the following plots (1, 2, 3, and 4). Considering first plot 1, containing the results at 25°, we find that the earlier results at this temperature are in general well confirmed. The initial values for $t = 0$, and the form of the curves agree well with those previously obtained, but the initial lag in the present series is less than in the former. This may be due to the fact that in the former experiments, the "stock" solution from which the dilutions were made, was three times as strong as the present "stock" solution. The "lag" is, however, unmistakable in the solution $C = 0.0075$.

On comparing plot 1 with plots 2, 3, and 4, the enormous effect of temperature on the reaction is at once evident. Whereas, the hour was a convenient unit for representing the data at 25°, the day must be used to represent the data at 0°, and the more concentrated solutions at 15°. It is seen, as was expected, that lowering the tempera-



PLOT 1.

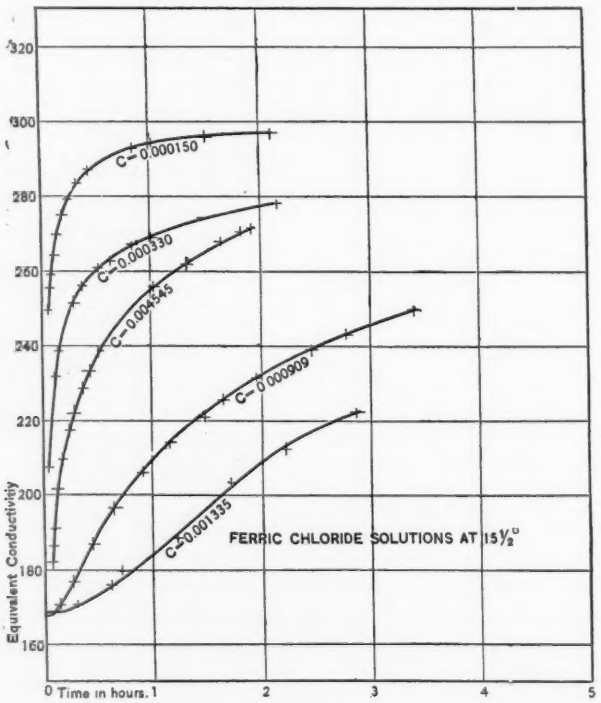
ture diminishes the rate of the reaction, increases its initial lag, and the time required to reach equilibrium. The form of the curves for equal concentration thus flattens out with decreasing temperature; the curves for the solutions at 25° approach in form, in fact almost coincide with, the curves for greater dilutions at lower temperatures. Thus compare:

at 25°.	at 15°.
$C = 0.0004545$.	$C = 0.00015$.
$C = 0.001335$.	$C = 0.0004545$.
$C = 0.00360$.	$C = 0.000909$.

A decrease of temperature of 10° from 25° has nearly the same effect on retarding the reaction as increasing its concentration about

three times; lowering the temperature to 0° retards the reaction as much as increasing the concentration fifteen to twenty times.

It is interesting to note how the solution $C = 0.001335$, which exhibits no lag at 25°, does not change appreciably until after about 5 minutes at 15.5°, and does not change until after a day at 0°. The solution $C = 0.0025$ remains unchanged at 0° until after 4 days, and it is probable that a solution of $C = 0.005$ which has a lag of a few hours at 15° would remain practically unchanged at 0°. The general expression for the rate of change as function of the temperature cannot, however, be determined from the data yet at hand.



PLOT 2.

In the course of the experiments a few observations were also made on the effect of temperature on the turbidity of ferric chloride solutions of certain concentrations when allowed to stand. This turbidity, which is probably due to the formation of oxychloride was found by Goodwin to be accompanied by a corresponding change in

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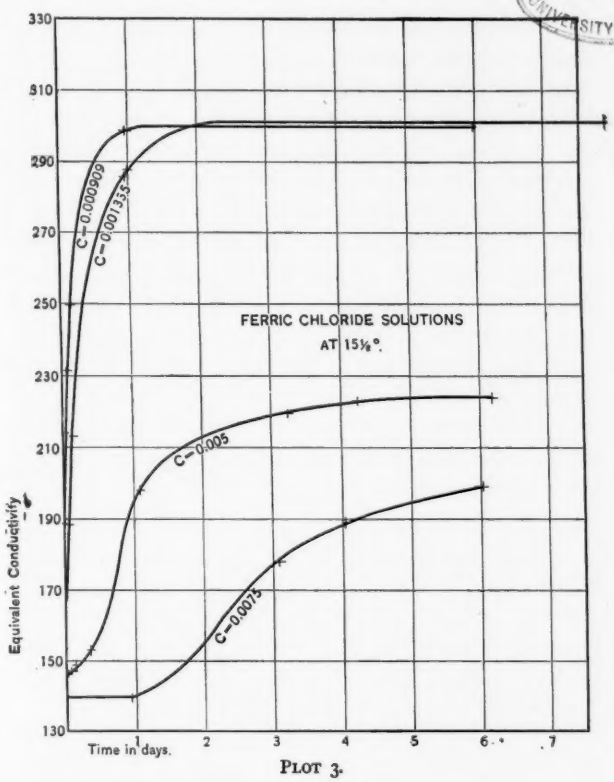
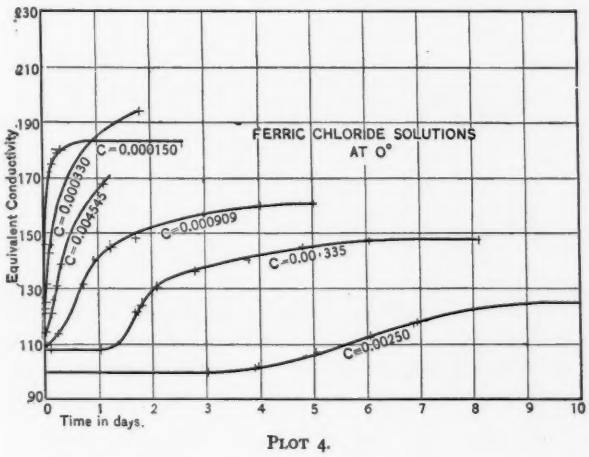


PLOT 3.



PLOT 4.

conductivity of the solutions and to have a "lag" dependent on the concentration of the solution.

Thus a 0.09 normal solution became turbid only after the lapse of 2 weeks, while a solution ten times as dilute became turbid in about a day. On the other hand, a solution 0.0057 normal remained perfectly clear even after 2 weeks, thus showing that the precipitate was formed at 25° only within narrow limits of concentration.

In the present investigation, solutions of strengths 0.02, 0.01, 0.004, and 0.002 normal were found to remain perfectly clear for at least 2 weeks when kept in ice. A 0.0075 normal solution on the other hand, became very turbid at 25° in less than 4 days, slightly turbid in the same time at 15° (very turbid after 6 days), while it remained clear at 0°.

Lowering the temperature thus greatly tends to diminish the separation of oxychloride from the solution as well as to prevent the formation of colloidal hydrate.

Effect of Colloidal Ferric Hydrate on the Reaction.

To test whether the hypothesis, previously advanced to account for the accelerated rate of the reaction when once started, was verified by experiment, various amounts of previously prepared Graham's colloidal ferric hydrate were added to dilute solutions of ferric chloride, and the change in conductivity then followed as in the previous experiments. A solution 0.0075-equivalent normal, and a temperature of 25° were chosen, as the preceding experiments showed that at this temperature a solution of this strength had a marked initial lag of about 20 minutes. A known amount of best distilled water was weighed out in a 250 c.c. bottle, brought to a temperature of 25°, and a known small amount of the colloidal ferric hydrate added with a pipette. The specific conductivity of this solution was then determined. At a noted time a measured amount of ferric chloride solution was added, the whole vigorously shaken, the "plunge" electrodes replaced, and the change in conductivity then followed at known intervals of time.

In the following Tables, XX, XXI, XXII and XXIII, are given the results obtained. Under "equivalent conductivity" is given the conductivity of the ferric chloride in the mixed solution after correcting for the conductivity of the added colloidal ferric hydrate in the

solution. This had an appreciable conductivity, as already stated, due to the presence of some crystalloids still remaining in it. In Table XXIII, however, the values given are the uncorrected conductivity values for the mixture — the specific conductivity of the colloidal solution not having been in this case accurately determined. A comparison of the initial corrected values in Tables XX, XXI, and XXII, namely, 172.6, 171.2, and 172.6, with the initial value found for the pure ferric chloride solution 172.8 (Table VI), shows that they agree almost exactly, whence it is safe to conclude that the conductivity of the mixture may be assumed additive. We have, therefore, for convenience of comparison in plotting, corrected all the values given in Table XXIII by — 8, thus reducing the initial values of the conductivity of the ferric chloride to that found in the other solutions.

TABLE XX.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.000116$. $t = 25.0°$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 20	172.6	13 40	174.9
2 20	172.8	34 20	177.8
3 50	173.3	36 0	178.1
5 15	173.6	46 10	179.5
6 45	173.9	54 0	180.8
8 20	174.1	1 5 0	181.7
9 30	174.2	.....	.....

TABLE XXI.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.000232$. $t = 24.96°$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 35	171.2	54 50	186.1
3 5	172.4	1 15 0	192.6
4 30	172.7	1 36 0	199.0
6 35	173.2	1 40 0	200.0
7 40	173.6	3 31 0	222.2
10 50	174.3	3 36	223.2
25 20	177.8	23 51	262.6

TABLE XXII.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.00116$. $t = 24.96°$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 30	172.6	29 50	200.7
4 45	176.0	40 30	207.3
5 30	176.9	46 30	211.9
13 0	184.8	.....	.....
20 30	192.5	19 5	277.1

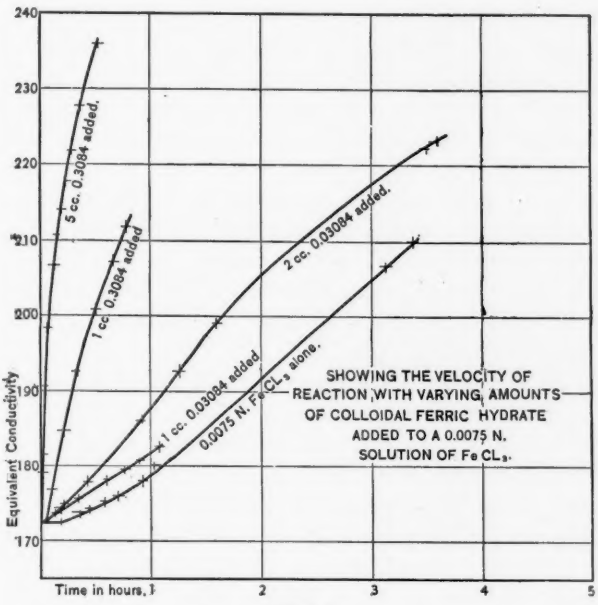
TABLE XXIII.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.00580$. $t = 25.0°$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
50	180.4	11 15	222.0
1 15	187.0	13 45	225.8
2 15	197.0	16 40	229.7
2 35	198.6	19 20	232.5
3 5	200.7	22 10	235.8
3 35	203.0	31 0	244.0
4 5	204.8	1 2 20	257.5
4 30	206.3	1 41 0	267.4
5 15	208.3	4 15 0	284.6
6 15	211.2	.....	.....
7 35	214.7	21 32	312.1

The effect of the presence of increasing amounts of colloidal hydrate on the course of the reaction is most readily seen from plot 5, made from the data in the preceding tables.

It is seen at once from this plot that, as anticipated, the presence of colloidal hydrate accelerates the reaction to a very marked extent. In all cases the reaction starts immediately upon diluting the chloride, the initial lag of 20 minutes observed in the neutral solution being thus completely absent. Moreover, the increase in the initial rate of the reaction is approximately proportional to the concentration of the added colloidal hydrate. This in the four solutions investigated is present in the ratio, 1 : 2 : 10 : 50, while the increase of conductivity per minute is approximately in the ratio of 0.2 : 0.4 : 1.4 : 10, or 1 : 2 : 7 : 50. The first three values are the rates during the first 5 or 6 minutes of the reaction; the last, during a still shorter interval of $2\frac{1}{2}$ minutes, as this last reaction slows up very quickly after the first few minutes. It seems probable, therefore, that other things



PLOT 5.

being equal, the presence of colloidal hydrate exerts a catalytic action nearly proportional to its concentration.

III.

EFFECT OF A MAGNETIC FIELD ON THE RATE OF THE REACTION.

It has now been pretty well established[1] that chemical reactions may in certain cases be modified when they are caused to take place in a powerful magnetic field. Wiedemann[2] has further shown that the magnetic moment of a ferric chloride solution is much diminished by the formation of colloidal ferric hydrate. It was therefore thought to be not without interest to investigate whether or not the velocity of the colloidal formation studied above was in any way affected by a magnetic field. As our experiments gave only negative results, the

[1] Wiedemann's Lehre von der Electricität for the early literature, vol. 3, p. 1129; Liesesang, Beibl. **15**, 123; Braham, Beibl. **16**, 304; Andrews, Proc. Roy. Soc. **52**, 114, 1892; Nichols, Am. J. of Sc., **31**, 372.

[2] Lehre von der Elect., vol. 3, p. 964.

numerous preliminary experiments and arrangements of apparatus will be passed over, and only the final arrangement briefly described.

It was desired to compare the rate of the colloidal formation in two exactly similar solutions at exactly the same temperature, the one placed in a strong magnetic field, the other removed from it. Any ordinary form of thermostat was of course out of the question, on account of the small distance between the poles of the electro-magnet between which it was desired to place the cell. We arranged, therefore, as thermostats, two duplicate Beckmann boiling-point tubes, provided with condensers and containing pure ether, boiling at 33° C., and used test tubes fitted into these ether jackets and provided with plunge electrodes as conductivity cells.

One of these was set up between the poles of a powerful electro-magnet, and the other at some distance away. Direct experiment then showed that the temperatures of aqueous solutions placed in the cells could be kept the same to 0.01° for several hours. The procedure was to allow the ether to boil for some minutes in both thermostats in order to bring the dry cell and electrodes placed therein to the proper temperature; to then dilute the ferric chloride to the desired strength in a separate flask containing water previously weighed and heated to the boiling point of ether; and then to quickly transfer the solution thus prepared to the two measuring cells.

TABLE XXIV.

$C = 0.0040$ approximately.

h.	m.	s.	$k \times 10^{-4}$ I.	$k \times 10^{-4}$ II.	h.	m.	s.	$k \times 10^{-4}$ I.	$k \times 10^{-4}$ II.
3	59	30	Diluted.		4	20	30		8.01
4	4	45		6.95		21	10	8.04	
	5	30	7.12			23	30		8.10
	6	50		7.22		24	0	8.12	
	7	15	7.29			26	35		8.16
	7	50		7.30		29	0	8.26	
	8	50	7.38			32	5		8.29
	9	25		7.50		32	50	8.33	
	10	5	7.53			39	20		8.43
	10	50		7.60		40	15	8.44	
	12	0	7.66			47	50		8.53
	13	0		7.69		48	30	8.54	
	14	20	7.78		5	6	5		8.70
	14	50		7.79		8	0	8.71	
	16	15	7.87			11	20		8.72
	17	0		7.88		13	20	8.75	
	17	35	7.93			14	30		8.75
	18	55		7.96					
	19	40	7.99						

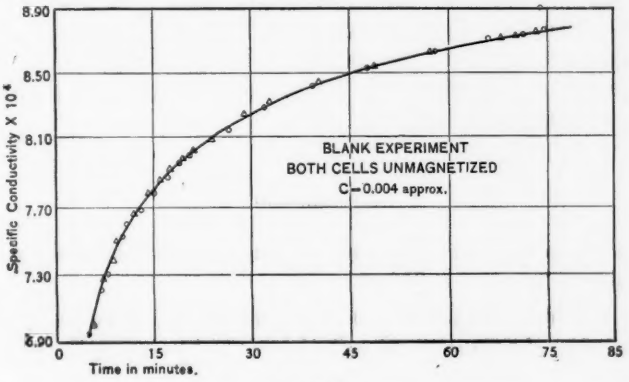
TABLE XXV.

$C = 0.0040$ approximately.

h.	m.	s.	$k \times 10^{-4}$ I.	$k \times 10^{-4}$ II.	h.	m.	s.	$k \times 10^{-4}$ I.	$k \times 10^{-4}$ II.
			Diluted.		2	3	50	8.14	
1	37	0				4	20		8.12
1	40	45	6.50			6	20	8.19	
	41	50		6.63		7	0		8.20[1]
	42	25	6.78			10	15	8.29	
	42	55		6.81		10	55		8.30[1]
	43	25	6.91			16	55	8.43	
	44	0		6.94		17	35		8.43[1]
	44	40	7.04			24	0	8.54	
	46	35		7.22		24	35		8.55[1]
	47	15	7.29			27	35	8.59	
	47	45		7.32[1]		28	5		8.60[1]
	48	55	7.42			41	50	8.75	
	49	30		7.46[1]		42	25		8.76[1]
	50	55	7.56			45	55	8.79	
	52	20		7.61[1]		46	15		8.80[1]
	54	40	7.79		3	6	25	8.93	
	55	10		7.79	3	7	0		8.94[1]
	58	30	7.95						
2	0	0		7.99					

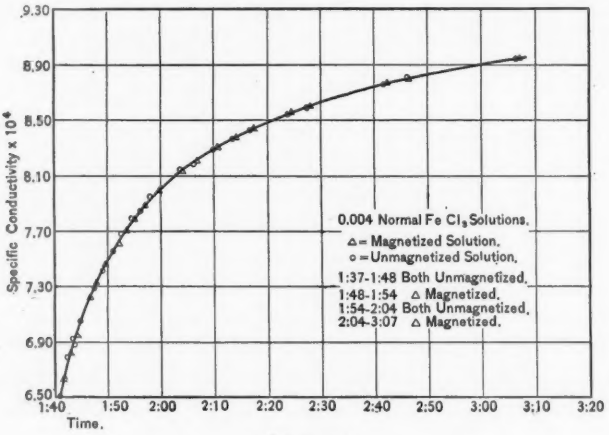
[1] Signifies that II was in the magnetic field.

The current in the electro-magnet could be regulated and thrown on or off at will. The strength of the field in which the solution was placed was determined by the change of resistance of a bismuth coil of wire placed in the field. The strength of field was thus found to be about 1,850 lines per square cm. Table XXIV contains the results of a blank run, both cells being unmagnetized. The values given



PLOT 6.

are specific conductivities at the temperature of boiling ether (33°). They are shown in plot 6, where it is seen that the two curves practically coincide throughout, thus confirming the accuracy of the cell constants and the constancy of temperature of the ether jackets. Table XXV contains the results of a run in which one cell remained unmagnetized, the other alternately magnetized and unmagnetized. The results of both series are shown in plot 7. The curves coincide



PLOT 7.

throughout, showing that no change in the rate of reaction was produced by the magnetic field. Numerous other runs confirmed this result, so that the conclusion may be drawn that the rate of formation of colloidal hydrate in ferric chloride solutions is not affected by the presence of a magnetic field of strength not greater than about 2,000 lines per square cm.

CONCLUSION.

The principal results of this investigation may be summed up as follows:

1. The effect of lowering the temperature is to very greatly diminish the rate of formation of colloidal ferric hydrate, and to increase the initial lag in the reaction.

2. The hypothesis previously advanced to account for the acceleration of the reaction when once started is confirmed. The presence of colloidal hydrate exerts a very marked catalytic action, causing the reaction to be accelerated by an amount approximately proportional to the amount of colloidal hydrate present in the solution.

3. No effect of a magnetic field could be detected on the course of the reaction.

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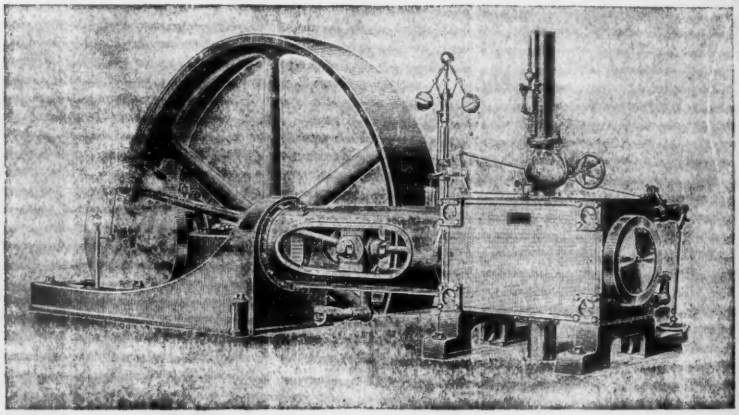

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